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STUDIES IN CHELOMETRIC AND PHOTOMETRIC TITRATIONS INCLUDING DESIGN AND CONSTRUCTION OF A PHOTOTITRATOR

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SUMMARY

Selectivity in chelometric titrations is achieved by controlling certain important factors. In general, these factors are the nature of the chelon itself, the pH of the solution, the presence of masking agents, and the method of end point detection. In the present study, "low stability masking" (i.e. masking via the formation of relatively weak complexes) and the photometric method of end point detection have been investigated and applied to the cadmium-zinc system. This system is difficult to resolve by any other titrimetric technique. The following methods have been developed: a consecutive photometric titration of cadmium and zinc, selective titrations of zinc in the presence of cadmium to visual and photometric end points, and a visually indicated titration for both cadmium and zinc in the same solution.

Due to certain limitations in the available instrumentation for photometric titrations, the design and construction of new phototitrator has been undertaken.

Consecutive Titration of Cadmium and Zinc

Microgram amounts of cadmium and zinc can be determined from a single titration curve in the following manner: The sample is adjusted to pH 9.4 with an ammonia-ammonium chloride buffer so that the total ammonia concentration is 0.01-0.03 F. Zincon is added to attain a concentration of 0.06-0.18 mg/ml. The titration is per-

formed photometrically at about 620 nm with [ethyleneglycolbis-(nitriloethyl)]tetraacetic acid (EGTA) as the titrant. The titration curve obtained shows two breaks which allow the determination of both cadmium and zinc. The influence of calcium impurities in the reagents used has been studied and a pretitration method is proposed to deal with small calcium blanks. If calcium is present or is added to the sample in an amount approximately equivalent to the other metals, an improved titration curve is obtained. This curve shows three breaks which are related to the consecutive titration of cadmium, calcium, and zinc.

Titration of Zinc in the Presence of Cadmium

Zinc can be titrated with (ethylenedinitrilo)tetraacetic acid (EDTA) at pH 5 by using Xylenol Orange as indicator. Cadmium can be masked by iodide; depending on the concentration of cadmium, up to 50% w/v potassium iodide is necessary. Correct results and good end points are obtained with cadmium:zinc mole ratios up to 300. Interferences by and tolerable limits in concentrations of some other metal ions have been investigated.

Photometric Titration of Zinc in the Presence of Cadmium

Zinc can be titrated in the presence of large amounts of cadmium and some other metals in the following manner. The sample is neutralized and buffered to pH 5.0 with an acetate buffer. Potassium iodide (up to about 60% w/v, depending on the cadmium concentration) and Xylenol Orange indicator are added and the titration

is performed photometrically at about 570 nm with (diethylenetrinitrilo)pentaacetic acid (DTPA) as titrant. Correct results have been obtained with cadmium:zinc ratios up to 3300. Interferences by and tolerable limits of concentrations of some other metal ions have been investigated.

Titration of Cadmium and Zinc in the Same Solution

Both Cadmium and zinc, when present in approximately equal amounts, can be determined in the following manner: At first, the sum of cadmium and zinc is titrated with EDTA at pH 6.1 with Xylenol Orange as the indicator. Potassium iodide is then added to mask the cadmium, the pH is lowered to about 5.0, and the EDTA released by the masking of cadmium is back-titrated with standard zinc solution. Good results were obtained for cadmium:zinc ratios between about 20 and 0.05.

Construction of a New Phototitrator

The principal differences in the requirements of a photometer and a phototitrator are discussed and it is shown that an instrument specifically designed for photometric titrations is more versatile than a modified photometer. The prime requirements for a phototitrator are operation with the titration vessel in ambient light, freedom from the need for special cuvettes, and the possibility of adjusting the light path length by some means other than changing vessels.

A simple yet versatile phototitrator which meets these requirements is described. Operation in ambient light is achieved by utilizing the principle of focussing the light beam on an extremely

small photodetector. The other two requirements are met by the following construction: the light enters the titration solution via the immersed end of a tube which is closed at its lower end with a flat glass plate, passes through a length of solution, leaves the solution through the bottom of the titration vessel, and, after passing through the monochromating device, is focussed on the photodetector. Thus vessels of greatly different sizes and shapes can be accommodated and the path length can be adjusted within wide limits by changing the depth of the immersion of the light conducting tube. Constructional details for the apparatus are given as well as the results of various tests performed.

CHAPTER I

INTRODUCTION

Some Definitions

Since there is no uniformly accepted terminology in the field of chelometric titrations, it will be helpful to preface this discussion with a few definitions. These definitions may differ in some respects from those found in other literature but they will be applied uniformly throughout this report.

A metal complex is a species formed by the replacement of one or more water molecules coordinated to a metal ion in solution by other molecules or ions. The species replacing the water is called a ligand. A ligand which occupies only one coordinating position on the metal ion is said to be unidentate ("one toothed"). Similarly, a ligand which is capable of forming two bonds to the metal ion is said to be bidentate; a ligand forming three bonds is tridentate; etc. In general, a polydentate ligand is capable of occupying several coordination positions on the ion. The term chelate compound, introduced by Morgan and Drew (1), denotes a particular type of complex which involves a polydentate ligand. In a chelate compound, the metal ion is a member of one or more rings; these rings are usually five-membered in the analytically important complexes. The word chelon is the generic name for a special class of chelating agents (polyaminocarboxylic acids) which

form stable, water soluble complexes with metal ions. Metal-chelon complexes are usually 1:1. The term complexometric titration refers to any titration which is based on a complexation reaction. Chelatometric titrations are complexometric titrations which involve the use of polydentate ligands. Chelometric titrations are a special class of chelatometric titrations and are based on the use of chelons. Often, in the literature, no distinction is drawn between complexometric, chelatometric, and chelometric titrations, although most of the methods reported to date have, in fact, been chelometric methods.

Historical Review

The first application of a complexation reaction to titrimetry was reported by Marozeau in 1832 (2). In that method, iodide is titrated with mercury(II) to form HgI_4^{2-}; the end point is indicated by the precipitation of HgI_2 according to

$$Hg^{2+} + HgI_4^{2-} = 2\ HgI_2$$

Prior to 1946, the only other widely accepted complexometric titrations were those of cyanide with silver (3) and of nickel and copper with cyanide (4,5).

The history of chelometric titrations begins in 1945-6 with the introduction by Schwarzenbach of (ethylenedinitrilo)tetraacetic acid (EDTA) as a titrant for metal ions (6,7,8). EDTA forms stable, 1:1 complexes with most polyvalent metal cations and has found application to the determination of many of these. Chelometric

titrations involving EDTA and related compounds have become increasingly important in recent years and the literature in the field already numbers several thousand publications. The scope of chelometric titrations as well as the theoretical aspects and the more important applications have been reveiwed recently by Schwarzenbach and Flaschka (9).

The Stability Constant

The equilibrium constant for a complexation reaction is the same as the stability constant of the complex formed in the reaction. The stability constant is an important parameter in estimating the feasibility of a titration based on complex formation. For the purposes of analytical chemistry, a constant written in terms of concentrations is desirable. Thus it is common practice to operate with concentration constants rather than thermodynamic constants. In fact, the stability constants of most complex compounds are nowadays usually determined as concentration constants at a given ionic strength. Ringbom (10) has shown that the effect of changes of ionic strength on concentration constants can usually be neglected in the range between μ = 0.1 and 0.5 — a range in which many constants have been measured and where chelometric titrations commonly are performed.

Of the several types of stability constants the thermodynamic constant is mostly of interest to physical chemists. This constant is expressed in terms of activities of the participating species and is related to the Gibbs Free Energy change of the

reaction. A second kind of constant, the absolute constant, is one type of concentration constant. If a metal M and a chelon Y react to form a complex MY, the absolute stability constant relationship is

$$K_{abs} = \frac{[MY]}{[M][Y]}$$

where the brackets indicate molar concentrations. Charges are omitted for simplicity. Only the concentrations of "free" metal ion (i.e. metal ion which is present as the aquo complex), fully dissociated Y, and complex MY are used in the expression for the absolute constant. The use of the absolute constant in calculations is complicated by the fact that the many possible side reactions can affect these concentrations. For instance, protonation of the ligand, reactions of the metal with other complex-formers, and formation of mixed complexes of the type MZY must often be taken into account.

An ingenious and elegant approach, introduced by Schwarzenbach (11) and later extended by Ringbom (10) involves the use of conditional stability constants. The conditional stability constant (sometimes called the apparent or effective constant) is written as a function of the total (analytical) concentrations of the complex MY and of the metal and chelon which have not participated in the main reaction. It reflects the effects of any competing equilibria (side reactions) and is related to the absolute constant by an easily calculated factor. When conditional constants are used, all titration calculations can be performed as if nothing but

the main reaction were taking place.

A fourth kind of constant, the mixed constant, involves both activities and concentrations in the stability constant expression. Some concentrations, especially hydrogen ion concentrations, are usually measured potentiometrically and it should be noted that potentials indicate activities rather than concentrations. Thus, if concentration constants are used, all potentiometrically determined pH values demand a correction. This correction can be avoided by the use of mixed constants. In a mixed constant, the equilibrium expression contains hydrogen ion and hydroxide ion activities but concentrations of all other species. Both absolute and conditional constants can be written as mixed constants when the hydrogen or hydroxide ions are participants in the equilibrium.

The Calculation of Conditional Stability Constants

The conditional stability constant can be calculated from the absolute constant by applying a factor for each competing reaction. The calculations of these factors will be treated individually

The Influence of pH

Chelons are polyprotic acids and are present as completely dissociated anions only in strongly alkaline solution. At pH values below about 10-11, different amounts of the various protonated forms of a given chelon will be present. The relative amounts of these forms depends on the pH and the acid dissociation constants of the chelon. A factor, α_H, can be used to calculate the conditional

constant from the absolute constant. The subscript H denotes the fact that the hydrogen ion concentration dependence is being considered.

In the following discussions, all calculations will be made on the basis of molar concentrations, as symbolized by brackets, with the exception that hydrogen ion activity, denoted by parentheses, will be employed.

If protonation of the ligand is the only side reaction, the conditional stability constant is expressed for any pH as

$$K_{cond} = \frac{[MY]}{[M][Y]^*} \tag{1}$$

where $[Y]^*$ denotes the total concentration of chelon not combined with the metal, but including all protonated forms which may exist at a particular pH. Here, and throughout this discussion, charges are omitted whenever they are not required for clarity.

The quantity $[Y]^*$ is related to $[Y]$ by the defined relation

$$[Y]^* = [Y]\alpha_H \tag{2}$$

where $[Y]$ is the molar concentration of the completely dissociated chelon anion. Assuming that Y is a tetraprotic acid such as EDTA, a material balance gives

$$[Y]^* = [Y] + [HY] + [H_2Y] + [H_3Y] + [H_4Y] \tag{3}$$

It is possible to obtain expressions for the various terms in equation (3) by introducing the stepwise acid dissociation constants of the chelon. For practical purposes, however, it is more con-

venient to employ the reciprocals of the acid dissociation constants, namely the stability constants of the "proton complexes" of the chelon. For a tetraprotic acid such as EDTA, these expressions are

$$K_1 = \frac{[HY]}{(H)[Y]} \tag{4}$$

$$K_2 = \frac{[H_2Y]}{(H)[HY]} \tag{5}$$

$$K_3 = \frac{[H_3Y]}{(H)[H_2Y]} \tag{6}$$

$$K_4 = \frac{[H_4Y]}{(H)[H_3Y]} \tag{7}$$

It should be noted that the acid stability constant numbering is the inverse of the usual practice in numbering acid dissociation constants; i.e. K_4 corresponds to the first ionization constant, K_3 to the second ionization constant, etc. From the equations above, $[H_4Y]$ can be expressed in terms of K_4, $[H_3Y]$ in terms of K_3, and so forth. When these expressions are substituted into equation (3), the result is

$$[Y]^* = [Y] + K_1(H)[Y] + K_2(H)[HY] + K_3(H)[H_2Y] + K_4(H)[H_3Y] \tag{8}$$

Completing the substitution to replace all concentration terms other than $[Y]$ on the right side of (8) gives

$$[Y]^* = [Y] + K_1[Y](H) + K_1K_2[Y](H)^2 + K_1K_2K_3[Y](H)^3 + K_1K_2K_3K_4[Y](H)^4 \tag{9}$$

Division by [Y] and combination with equation (2) gives the desired expression for α_H:

$$\alpha_H = \frac{[Y]^*}{[Y]} = 1 + K_1(H) + K_1K_2(H)^2 + K_1K_2K_3(H)^3 + K_1K_2K_3K_4(H)^4 \qquad (10)$$

This last formula allows the calculation of α_H for any pH value if the four acid dissociation constants (and therefore their reciprocals) are known. It is convenient to calculate α_H at several different pH's and to prepare a plot such as Figure 1 for easy reference. When α_H is known, the conditional stability constant can be calculated by combining equations (1) and (2) with the expression for the absolute constant to obtain

$$K_{cond} = \frac{[MY]}{[M][Y]\alpha_H} = \frac{K_{abs}}{\alpha_H} \qquad (11)$$

or, in logarithmic form

$$\log K_{cond} = \log K_{abs} - \log \alpha_H \qquad (12)$$

It is of interest to note that the numerical value of α_H is <u>not</u> dependent upon the concentration of Y but, for a given chelon, is determined solely by the pH.

In the manner outlined above, calculations may be performed which allow the prediction of the effect of pH on a chelometric titration. For example, the logarithm of the absolute stability constant of the magnesium-EDTA complex is 8.7 and the value of $\log \alpha_H$ for EDTA pH 4.0 is 8.6 (10). Thus the logarithm of the

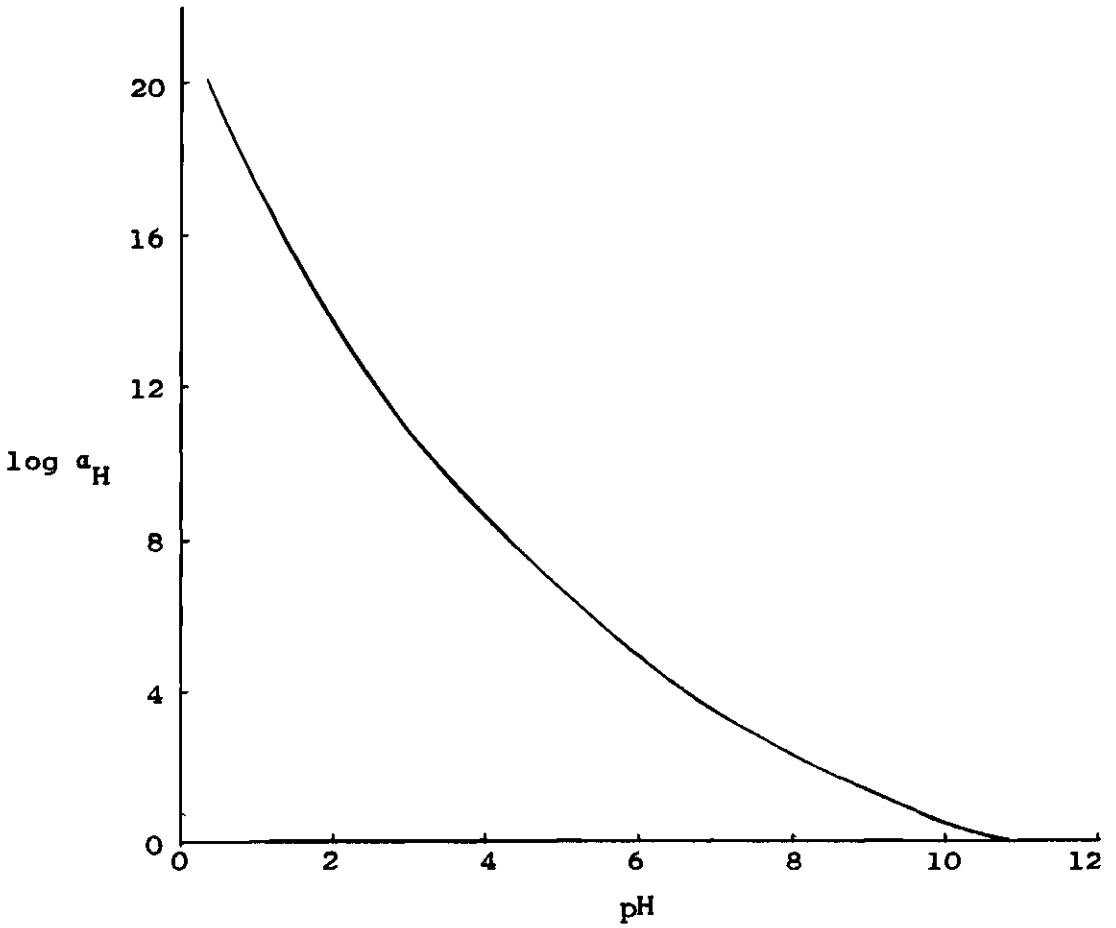

Figure 1

Log α_H for EDTA as a Function of pH

apparent constant of the Mg-EDTA complex at pH 4.0 is 8.7 - 8.6 = 0.1. At that pH, then, the Mg-EDTA complex is essentially completely dissociated and, for all practical purposes, magnesium will not react with EDTA.

The influence of hydroxo complexes on the conditional stability constant, while clearly pH dependent, is deferred until the next section because the mathematical treatment is analogous to that for auxiliary complex-formers.

The Influence of Other Complex-Formers

When a complex-forming substance other than the titrant is present, the metal ion present is distributed between the "free" aquated ion and the complexes formed with the titrant and the other complex-forming substance. The conditional stability constant which takes into account the influence of an auxiliary complex-former, Z, is given by

$$K_{cond} = \frac{[MY]}{[M]^*[Y]} \qquad (13)$$

where $[M]^*$ is the concentration of the metal ion not combined with the chelon, including the "free" metal ion and all complexes formed with Z. The relation between $[M]^*$ and $[M]$ is analogous to that in equation (2) and is given by

$$[M]^* = [M]\beta_Z \qquad (14)$$

Assuming that the complexes between M and Z are mononuclear (i.e. that there is only one M in each complex species) the total amount

of M which is not combined with the chelon is given by

$$[M]^* = [M] + [MZ] + [MZ_2] + \ldots + [MZ_n] \qquad (15)$$

Substitution of the stepwise stability constants of the various complexes formed between M and Z into equation (15) yields

$$[M]^* = [M] + K_1[M][Z] + K_1K_2[M][Z]^2 + \ldots + K_1K_2\ldots K_n[M][Z]^n \qquad (16)$$

Division by [M] and combination with (14) gives

$$\beta_Z = 1 + K_1[Z] + K_1K_2[Z]^2 + \ldots + K_1K_2\ldots K_n[Z]^n \qquad (17)$$

The expression for the conditional stability constant is then obtained from a combination of equations (13) and (14) with the expression for the absolute stability constant. The result is

$$K_{cond} = \frac{[MY]}{[M]\beta_Z[Y]} = \frac{K_{abs}}{\beta_Z} \qquad (18)$$

or, in logarithmic form

$$\log K_{cond} = \log K_{abs} - \log \beta_Z \qquad (19)$$

Note that [Z] is the concentration of the ligand not combined with the metal. The total concentration of Z can be taken to be equal to [Z] only if a sufficient excess is present so that the amount combined with the metal may be neglected. It is also important to realize that Z may be, and most often is, an acid or

base (e.g. acetate, ammonia, hydroxide) so that the concentration of free Z, [Z], is dependent upon the pH. This effect is easily calculated from the appropriate α_H for Z.

If several complex-formers are present in the solution, the overall β factor can be calculated according to

$$\beta_{total} = \beta_1 + \beta_2 + \ldots + \beta_p + (1-p) \qquad (20)$$

where p is the total number of β factors (10). Usually one or two of the factors will be significantly larger than the others and the other factors can then be neglected.

Other Influences

The value of the conditional stability constant is also affected by other metal ions which are present in the solution, by the formation of acid and base complexes of the type MHY and M(OH)Y, and by the formation of other mixed complexes of the type MZY. When such side reactions are important, their influence can be taken into account with factors which are calculated by a method analogous to those outlined above. It is of interest to note that, when such mixed complexes are formed, the factor multiplies into the numerator of the absolute stability constant. Since the minimum value of the factor is one, the formation of mixed complexes results in an increase in the numerical value of the conditional constant.

For a comprehensive treatment of conditional stability constant calculations and for extensive tabulations of factors for various side reactions, the reader is referred to the monograph by

Ringbom (10).

Stability constants are usually measured at a specified ionic strength (commonly 0.1) and temperature (often 20° or 25°C). By changing these parameters, the chemist can, within a narrow range, change the value of a conditional stability constant. For instance, increasing the ionic strength by means of addition of an inert electrolyte usually decreases the stability. The conditional constant can also be changed somewhat by adding organic solvents to the solution. At the present time, our knowledge is not sufficient to allow quantitative predictions regarding these effects. This is not an important drawback, however, since the effects are generally small. The results of changes in these parameters are usually important only in borderline situations, i.e. in cases where the stability constants are near the limits at which a titration becomes impossible.

Selectivity in Chelometric Titrations

A selective titration reaction can occur only if the side reactions of the titrant with foreign metal ions are prevented or suppressed. There are two general approaches; The first approach is the selection of a chelon which is intrinsically more selective. With a given chelon, the control of pH, the use of masking agents or kinetic effects, the variation of the mode of titrant addition or method of end point detection, or some combination of these may improve the selectivity.

The α and β factors are very useful in predicting the effects

of reaction conditions on selectivity. It is clear that two metal ions will only react in discrete steps if they differ considerably with respect to the conditional stability of their chelonates. It is then only necessary to be able to detect the end point of the titration of the first reacting metal. The requirement that a selective or specific set of indicators be available is met for some mixtures but, in general, is difficult to fulfill. The only alternative is recourse to an instrumental method of end point detection.

Selection of the Chelon

Few selective reactions are available solely on the basis of the structure of the chelon. All chelons are selective to some degree, however, and reaction conditions can be altered to enhance the inate selectivity of a given chelon.

The pH Effect

A change in solution pH often affects the relative stabilities of metal chelates. If the change increases the difference in the conditional stability constants of the chelonates of two metals, selectivity will be enhanced. As an example, consider the conditional stability constants of iron-EDTA and calcium-EDTA, shown in Figure 2 as functions of pH. The data are taken from Ringbom (10) and include the corrections for the formation of metal hydroxo complexes and mixed complexes of the types MHY and M(OH)Y. At pH 10, the difference in the stability constants is only 3.8 log units. At pH 3, however, the difference is 14.0 log units and a selective titration of iron in the presence of calcium is readily possible.

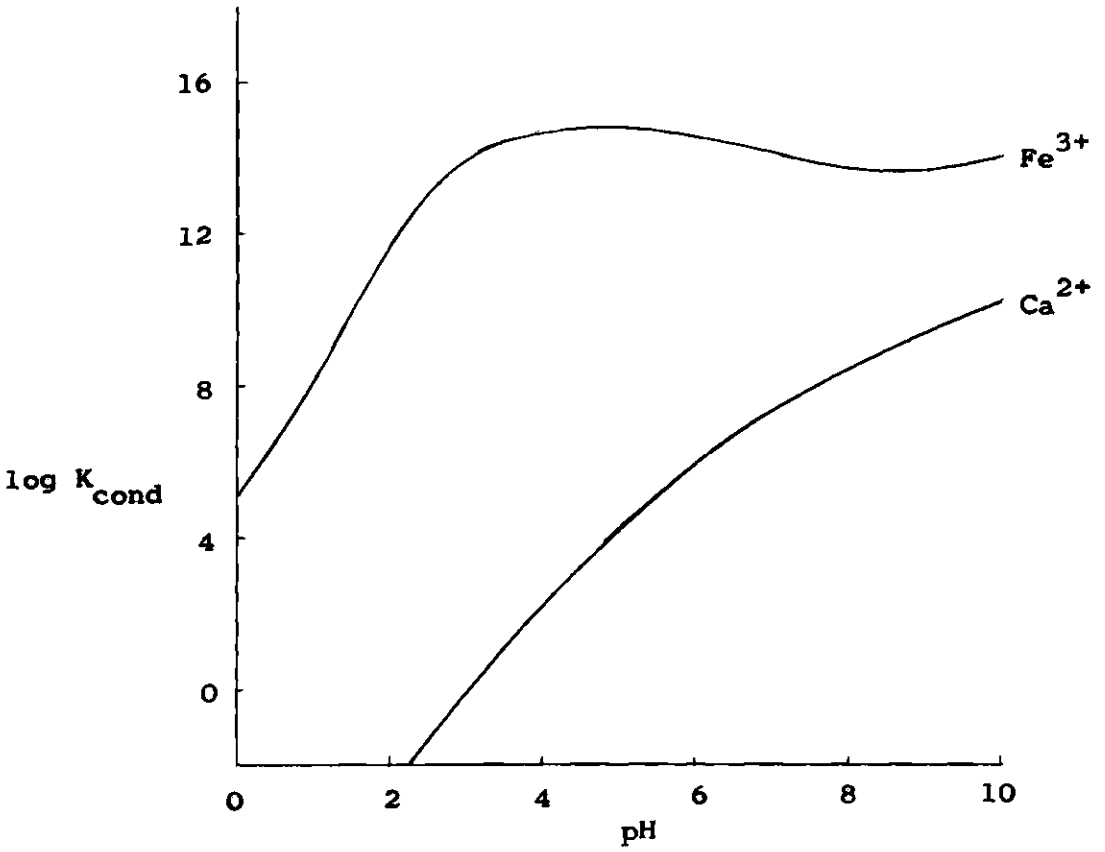

Figure 2

Effect of pH on the Conditional Stability Constants of Fe(III)-EDTA and Ca-EDTA

Masking

Masking is the means most often used to achieve selectivity in chelometric titrations. It is a process by which certain reactions of a substance are prevented. Masking implies that neither the substance being masked nor the reaction product(s) of the masking reaction is physically removed from the solution. As applied to titrations, these considerations imply that the masking reagent must decrease the conditional stability of the complex between titrant and foreign ion to the point where the latter ion does not interfere with the titration. The masking reagent should not adversely affect the main titration reaction.

In general, masking can be accomplished by one or a combination of the following processes:

(1) precipitation

(2) oxidation or reduction

(3) complexation

Masking via precipitation is subject to complication by coprecipitation and postprecipitation and only a few practical cases are known. The most famous example is the titration of calcium in the presence of precipitated magnesium hydroxide (8).

By converting a metal to a different oxidation state, a masking action can sometimes be achieved. Generally, metals in lower oxidation states form weaker complexes. For example, the logarithms of the absolute stability constants of the iron(II)- and iron(III)-EDTA complexes are 14.3 and 25.1, respectively (10).

The most widely applied masking reactions are complexation

reactions. For instance, cobalt, nickel, copper, zinc, and cadmium can be masked with cyanide to allow the titration of magnesium, lead, and some other metals at pH 10 with EDTA.

Cheng (13) has reviewed the use of masking reagents and has presented some principles which can be used in their evaluation.

One facet of masking which has not yet received wide attention is "low stability masking." Generally, masking by complexation is accomplished with moderate amounts of ligands which form relatively strong complexes with the foreign ion(s). On the other hand, low stability masking, as the name implies, involves the use of reagents which form relatively weak complexes. If the masking is to be effective, these reagents must necessarily be used in high concentrations. A part of the present study is devoted to the investigations of a new application of low stability masking (see Chapters VI, VII, VIII, and IX).

Kinetic Effects

Kinetic effects can be used to advantage if the reaction between an ion and the titrant is slow. For example, chromium(III) reacts quite slowly with EDTA in acid solution while iron(III) reacts quickly. Thus iron can be titrated in the presence of chromium (14) although the stability constants of chromium(III)-EDTA and iron(III)-EDTA are nearly equal. Similarly, nickel reacts slowly with EDTA but, at room temperature, the reaction is not quite slow enough to allow a "kinetic masking" of nickel. If, however, the solution temperature is lowered to $0^{\circ}C$, the decrease in the reaction rate of nickel is sufficient to prevent its complexation

with EDTA during the period required to titrate another metal ion (15).

Types of Titrations

Direct Titration. The most common approach to titrations is the direct addition of increments of a standard solution of chelon to the sample solution until the end point is reached.

Back-Titration. An excess of standard chelon solution is added to the sample solution and the excess is back-titrated with a standard solution of a suitable metal ion. This procedure is used when the titration conditions are such that the metal would be precipitated (e.g. as the hydroxide) or when no suitable indicator is available for the metal. The back-titration method is also applied to cases where a slow reaction occurs: First, an excess of titrant is added; then the solution is warmed to complete the complexation; and last, the excess of chelon is back-titrated.

Replacement or Substitution Titrations. In a replacement titration, a solution of a metal ion is treated with an excess of a metal complex which is less stable than the same complex of the metal to be determined. The second metal is quantitatively displaced and can then be titrated with a standard chelon solution. This method can be used for the determination of metals which do not form chelonates which are stable enough to permit a direct titration. For example, when $K_2Ni(CN)_4$ is added to a solution containing silver, nickel is quantitatively released according to

$$2\ Ag^{+} + Ni(CN)_4^{2-} = 2\ Ag(CN)_2^{-} + Ni^{2+}$$

The nickel released is then titrated with EDTA (16).

Method of End Point Detection

Some methods of end point detection are inherently more selective than others and their use allows a relaxation of the requirements for a successful titration. The subject is discussed in some depth in the next chapter.

CHAPTER II

END POINT DETECTION AND SELECTIVITY

Introduction

The method of end point detection governs the selectivity of a titrimetric procedure. In order to discuss the relationship between end point detection and selectivity, it is convenient to distinguish between logarithmic and linear titrations.

In a logarithmic titration, the titration curve is a plot of amount of titrant added (abscissa) versus a quantity related to the logarithm of one (or more) of the species participating in the titration reaction. Examples are potentiometric acid-base titrations (pH), precipitation titrations and complexation titrations (pM, i.e. -log [M]), and redox titrations (cell potential).

In a linear titration, the amount of titrant added is plotted versus some quantity which is directly proportional to the concentration of one (or more) of the participating species. Examples include conductometric titrations (conductance), amperometric titrations (diffusion current), thermometric titrations (temperature), and some types of photometric titrations (absorbance).

The end point of a logarithmic titration is located somewhere in the (hopefully) steep portion of the titration curve. The end point in a linear titration is found by the extrapolation of two essentially straight line portions of the curve. In order to elucidate the practical consequences of this situation, a complex-

ation reaction will be taken as an example.

For the complex equilibrium

$$M + Y = MY$$

the highest degree of dissociation occurs when M and Y are present in equivalent amounts, i.e. at the equivalence point and thus near the end point. Consequently the end point in a logarithmic titration must be located in the portion of the curve which is the worst with respect to dissociation. If the same titration is performed using a linear technique, one branch of the titration curve is established well before the end point. In this region, M, which is titrated, is present in excess and the equilibrium is shifted to favor complete reaction with the titrant. Thus any change in the plotted property tends to be proportional to the amount of Y added and an essentially straight line is obtained. Beyond the end point, Y is in excess and again a favorable shift of the equilibrium is realized. The region in the vicinity of the end point, where considerable curvature may exist due to extensive dissociation, is not used; instead, the two straight portions are extrapolated to an intersect which is taken as the end point. Due to this extrapolation, the requirements for a successful linear titration are less stringent than for a logarithmic titration.

Calculation of Titration Curves

The primary complication to the calculation of chelometric titration curves is the effect of side reactions. When conditional

constants are used, the calculation is considerably simplified. The titration curve is obtained by solving a set of simultaneous equations which, in the case of a chelometric titration, is composed of the stability constant expression

$$K_{cond} = \frac{[MY]^*}{[M]^*[Y]^*} \tag{1}$$

and the conservation relations

$$C_M = [M]^* + [MY]^* \tag{2}$$

$$C_Y = [Y]^* + [MY]^* \tag{3}$$

For simplicity, the stars (*) will be omitted hereafter. It is convenient to define the units at the abscissa in terms of a, the fraction titrated, which is given by

$$a = \frac{C_Y}{C_M} \tag{4}$$

For the purpose of this calculation, the effect of dilution by the titrant will be neglected.

From equations (3) and (4),

$$a = \frac{[Y] + [MY]}{C_M} \tag{5}$$

Solving (1) for [Y] and substituting into (5) gives

$$a = \frac{\frac{[MY]}{[M]K} + [MY]}{C_M} = \frac{[MY]}{C_M}\left(1 + \frac{1}{[M]K}\right) \tag{6}$$

Equation (2) can then be solved for [MY] and that expression, when substituted into (6) gives

$$a = \left[\frac{C_M - [M]}{C_M}\right]\left[1 + \frac{1}{[M]K}\right] \qquad (7)$$

Equation (7) is an explicit relationship between a and [M] in terms of the parameters C_M and K. It is possible to solve (7) for [M] as a function of a but the result is complicated since the above equation is quadratic in [M]. It is more convenient to treat [M] as the independent variable.

Some linear and logarithmic titration curves, calculated with the use of equation (7) are presented in Figures 3 and 4.

Visual End Point Detection

The visual detection of the end point in a chelometric titration is usually based on the recognition of a color change which occurs when the titrated metal is transferred between the indicator complex and the chelon complex. There is a formal similarity between acid-base titrations and chelometric titrations which can be extended to the detection of the end point. For an acid-base titration, a pH sensitive indicator is used. In a certain pH range, a proton is attached or released depending on whether the range is approached from a higher or lower pH. Since the protonized form of the indicator differs in color from the unprotonized form, a color change accompanies the reaction. For a chelometric titration, a pM sensitive indicator is used. In a particular pM range, the metal ion is attached or released depending upon whether the range is approached

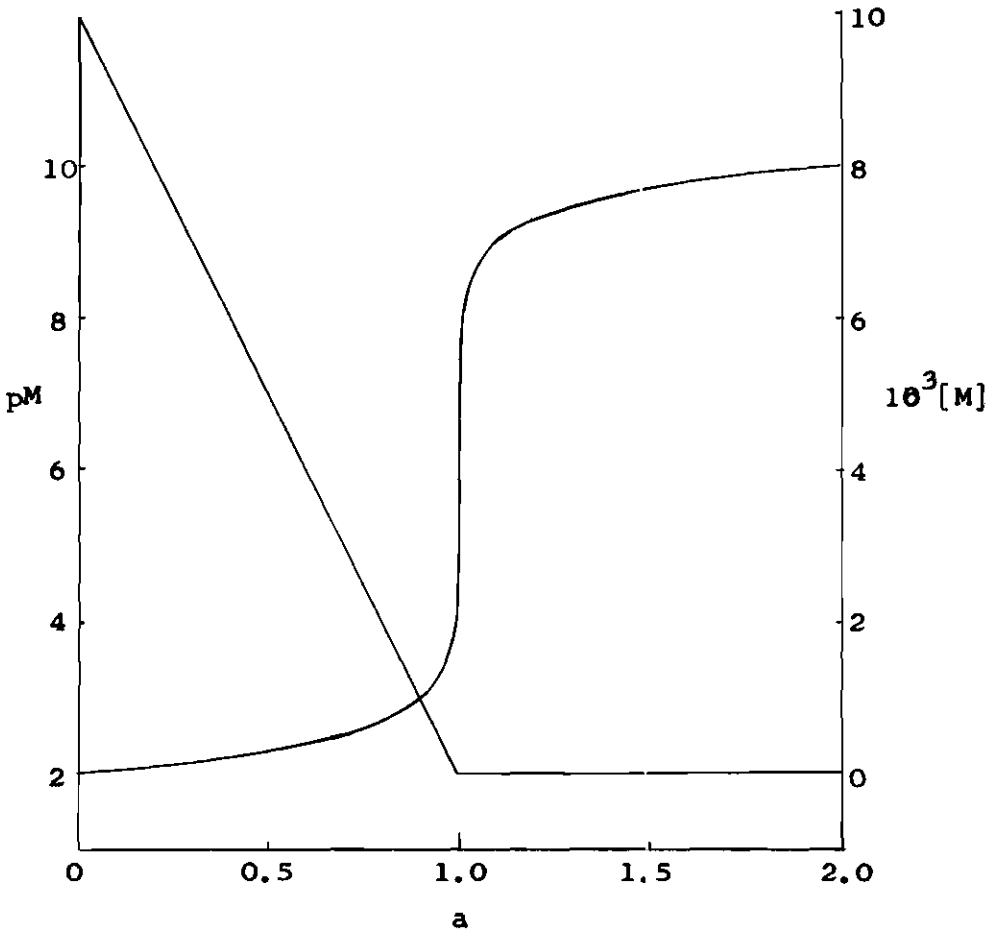

Figure 3

Calculated Linear and Logarithmic Titration Curves

$K_{MY} = 10^{10}$, $C_M = 10^{-2}$ F

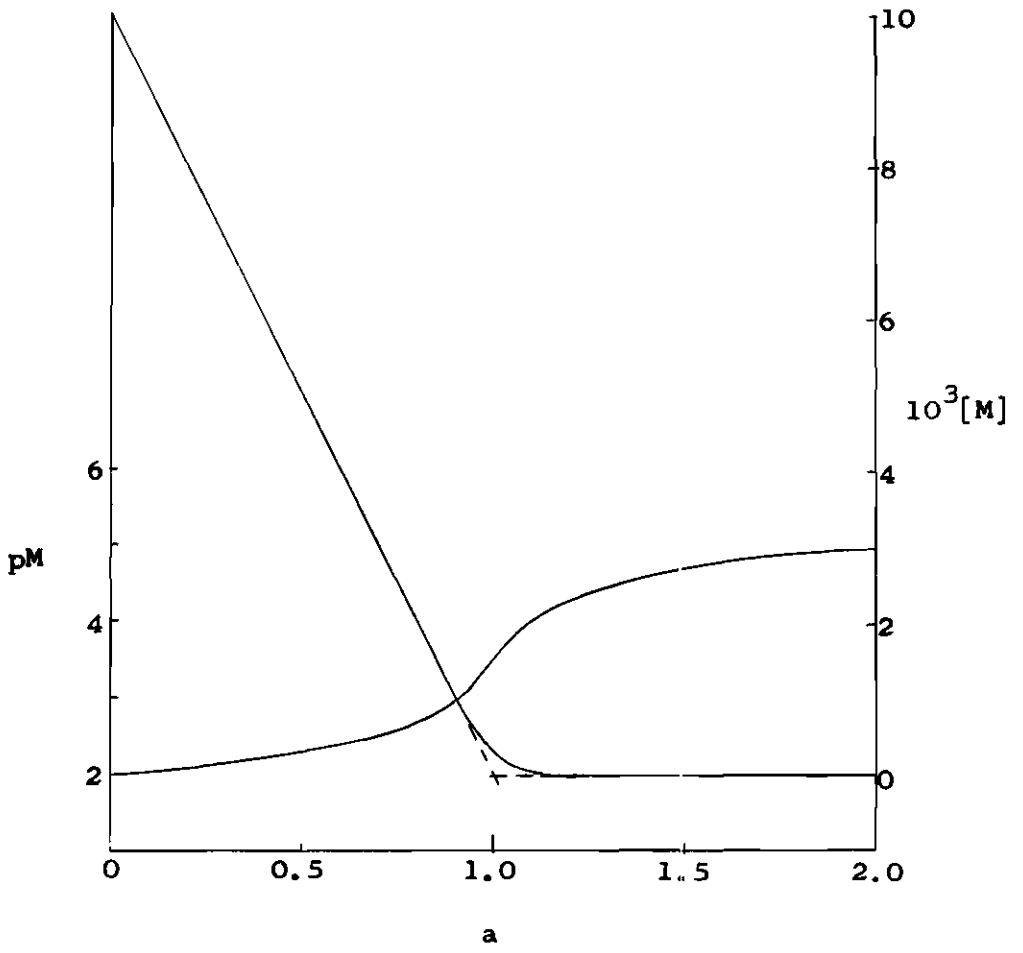

Figure 4

Calculated Linear and Logarithmic Titration Curves

$K_{MY} = 10^5$, $C_M = 10^{-2}$ F

from a higher or lower pM. Since the metallized form differs in color from the unmetallized form, this reaction is also accompanied by a color change. In both cases, the pH and pM ranges in which the indicators change color should be located in the steepest parts of the respective logarithmic titration curves. The ideal condition is obtained when the midpoint of the color change interval occurs at the inflection point of a curve, i.e. at the pH or pM corresponding to the equivalence point.

The situation in a chelometric titration is complicated by the fact that both pM sensitive indicators (also called metal indicators and metallochrome indicators) and the metal-indicator complexes can also act as acid-base indicators. This is a further reason for careful pH control in chelometric titrations. Another complication arises because most metal indicators are nonspecific. The effects of acid-base and complexation side reactions of indicators can be handled by calculation and use of the appropriate α and β coefficients.

Since the indicators respond to changes in pM, visual chelometric titrations can be considered to be logarithmic titrations. The detection of the end point depends upon the sharp jump in pM at that point. In well defined cases, such as the one illustrated in Figure 3, the pM at which the indicator changes color can lie anywhere in a wide range. As the conditional constant of the metal chelonate is lowered or as the metal ion conenctration is decreased, the pM jump becomes smaller and the indicator requirements become more stringent.

It can be shown that, in order to obtain a sharp end point, the ratio of the stability constant of the metal-chelon complex to the stability constant of the metal-indicator complex must be on the order of 10^4. Further, the value of the metal indicator constant must be greater than about 10^5. These numbers are obtained by the introduction of some simplifying assumptions into the formula obtained from a rigorous derivation (17). All the constants mentioned are, of course, conditional stability constants.

The selective, visual titration of metal M in the presence of metal N, when using indicator I which is specific for M, is possible when

$$\frac{K_M}{K_N} \geq \frac{K_I}{10^{-2}} \qquad (8)$$

K_M and K_N are the conditional stabilities of the metal-chelonates and K_I is the stability constant of the MI complex (18). Since K_I must be at least 10^5, it follows from equation (8) that the ratio K_M/K_N must be greater than about 10^7 if metal M is to be selectively titrated to a visual end point.

In some cases the pM change at the end point in a chelometric titration results in a change in the potential of a redox couple in the solution. This potential change can be indicated visually by a redox indicator. Redox indicators are seldom used, however, because of their sensitivity to small amounts of oxidizing and reducing impurities. Further, only a limited number of suitable redox indicators are known. Only a few practical applications of this indication

method have been developed (19).

Instrumental End Point Detection

The instrumental detection of the end point in chelometric titrations (as in titrimetry in general) often has significant advantages. If the use of an indicator is avoided, improved selectivity often results. Further, even when an indicator is present, the replacement of the human eye by a photocell (photometric titration) often allows a titration to be successfully performed where visual end point detection would be impossible.

Logarithmic Methods

The most commonly applied logarithmic titration is the potentiometric titration. When a reversible couple can be established with the metal to be titrated, the E.M.F. of that couple is given by the Nernst equation

$$E = E^{o} + \frac{2.303\ RT}{nF}\log [M]$$
$$= E^{o} - \frac{2.303\ RT}{nF}pM \qquad (9)$$

Thus the measured cell potential is directly proportional to pM and the titration curve is analogous to the pM curve.

For accurate detection of the end point, the voltage (pM) jump at the end point must be large. The height of this jump depends on both the metal ion concentration and on the value of the conditional stability of MY. Reilley (20) has defined a "titration factor," T, which furnishes a guide to the minimum value of the product $K_{MY}C_{M}$. The relation is

$$\log KC = T$$

The minimum value of T which will allow a potentiometric (or other instrumental logarithmic) titration is about four. The minimum T value for a visual titration is somewhat above five. Thus the conditions for a successful potentiometric titration are somewhat less stringent than for a visual indicator titration.

When a foreign metal ion is present, the effect can be taken into account with the α_N factor. A foreign ion has the effect of decreasing the conditional stability of MY and, thus, of decreasing the pM jump at the end point. As an example, consider the pM curve in Figure 3. Assume the same metal M is titrated in the presence of 10^{-2} M metal N whose chelonate has a stability constant of 10^7. The α_N is given by

$$\alpha_N = 1 + K_{NY}C_N = 10^5 \qquad (11)$$

Thus the conditional stability constant of MY is reduced to 10^5. The titration curve corresponding to that situation is presented in Figure 4.

K'_{MY}, the conditional constant of MY when N is present, and K_{MY}, the constant when N is absent, are related by

$$K'_{MY} = \frac{K_{MY}}{\alpha_N} = \frac{K_{MY}}{1 + K_{NY}C_N} = \frac{K_{MY}}{K_{NY}C_N} \qquad (12)$$

Thus, from equation (10),

$$\log \frac{K_{MY}C_M}{K_{NY}C_N} = T \qquad (13)$$

These considerations imply that a logarithmic titration, if executed instrumentally, can be performed successfully when the ratio K_{MY}/K_{NY} is as low as about 10^4 (for equal concentrations of M and N).

Linear Methods

The linear methods most often applied to the detection of end points in chelometric titrations are amperometry, photometry, and conductometry. Each of these methods has its own advantages and limitations and each, in selected applications, offers increased selectivity over logarithmic methods.

The titration factor for linear methods can be as low as about two (20). Thus, from the same considerations which were applied in the logarithmic case, the ratio K_{MY}/K_{NY} can be as low as 10^2 (for equal concentrations of M and N) in a linear method. It is therefore clear that linear methods of end point detection may be applicable to titrations which are impossible with logarithmic end point detection. For example, if the low stability constant of MY in Figure 4 were due to the presence of a foreign ion, the data show that a selective titration of M would be possible with a linear method although no end point could be detected with a pM method.

CHAPTER III

PHOTOMETRIC TITRATIONS

Theoretical Background

The basis for the photometric titration method is the Lambert-Beer Law for the absorption of monochromatic radiation

$$A = abc$$

where A is the absorbance, a is the absorptivity of the absorbing species at the wavelength used, l is the length of the light path through the absorbing medium, and c is the concentration of the absorbing species. For the photometric titration, the important consequence of this law is the linear relationship between concentration and absorbance.

The shape of a given photometric titration curve depends on the absorptivities of the titrand, titrant, and the reaction products. The wavelength is chosen from the absorbance spectra of these species. Usually the wavelength selected is the one at which the greatest possible absorbance change will be obtained during the titration.

Types of Photometric End Points

Flaschka and Sawyer have proposed a nomenclature for the three types of photometric indication (21). Both optical and equilibrium properties have been considered. The discussion here will be limited

chelometric titrations in which a 1:1 complex is formed.

Self-Indication. A system is said to be self-indicating when, upon addition of titrant, a metal ion initially present as a complex (perhaps the aquo complex) is progressively transferred into a chelonate of differing absorptivity. A linear titration curve, such as the one shown in Figure 5, is obtained.

Step-Indication. The term step-indication is used in reference to systems in which a complex-forming indicator is employed to obtain a step-like change in absorbance in the equivalence point region. Step-titrations are linear titrations in that the absorbance is a linear function of the concentrations of free and metallized indicator. The indicator, however, responds to the pM jump at the equivalence point so that photometric titrations with step-indicatinn should be classed as logarithmic or, at lease, quasilogarithmic titrations.

Figure 5 also presents a typical step-indication titration curve. Often, only one end of the step is sharp while the other end is greatly rounded; a curve of this type is often called a break point titration curve. The requirements for successful step-indication are similar to those for visual indication but are generally less stringent.

Slope-Indication. A system is termed slope-indicating when the end point is located via a self-indicating system, the metal of which is titrated after the metal to be determined. A typical curve is presented in Figure 5. The equilibrium requirements are those for a selective linear titration of the metal to be determined. In

addition, the absorptivities of all species involved must be such that the slopes of the titration curve before and after the end point differ sufficiently to permit precise location of that point.

One of the first studies of a slope-indicating system was performed by Underwood who investigated the EDTA titration of bismuth using copper as the slope-indicator. A titration curve for that system is similar to curve III in Figure 5. The first, horizontal segment corresponds to the transfer of bismuth from the aquo to the EDTA complex, neither of which absorbs. After all of the bismuth has been titrated, copper is complexed by the EDTA and the absorbance increases due to the relatively high absorptivity of the copper-EDTA complex. If desired, copper can also be determined by continuing the titration to a second end point since, when all the copper has been titrated, a second horizontal segment is obtained corresponding to the addition of colorless EDTA. Thus is is possible to determine two metals, bismuth and copper in this case, from a single titration curve.

Applications

In general, photometric end point detection is advantageous when applied to the titration of solutions which are dilute or in which the titration reaction tends to be appreciably incomplete at the end point, e.g. in neutralizations of very weak acids and bases, redox reactions involving couples with nearly equal potentials, complexation reactions in which rather weak complexes are formed, and in those reactions which are kinetically slow in the vicinity of

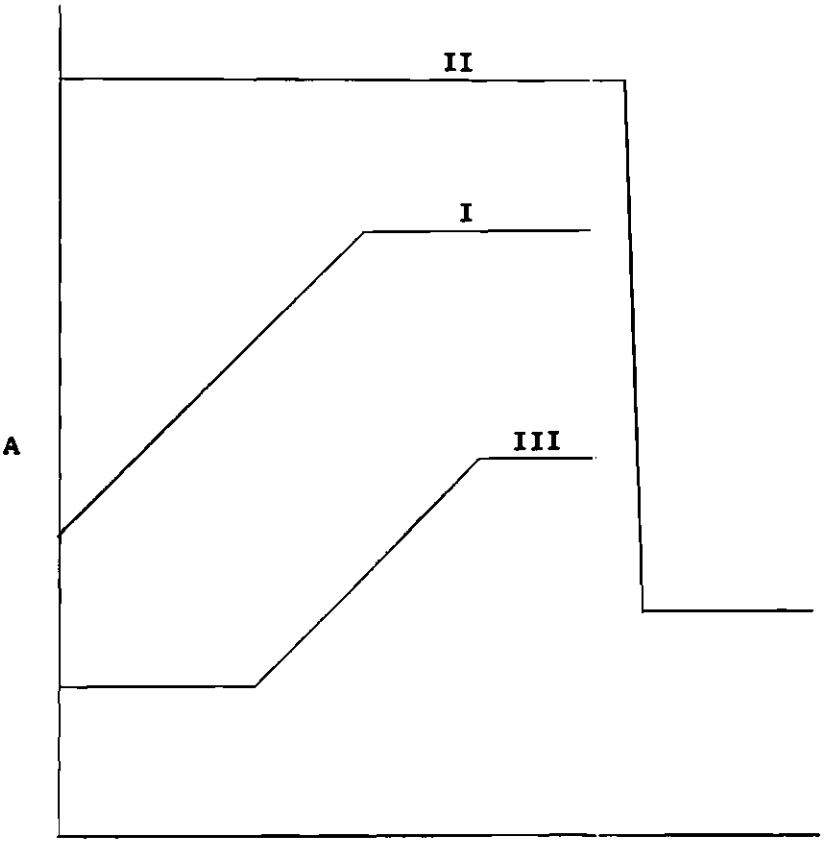

Figure 5

Idealized Photometric Titration Curves for Various Types of Indication

I. Self-Indication
II. Step-Indication
III. Slope-Indication

the equivalence point. All these circumstances tend to produce a rounding of the end point breaks but such rounding, if restricted to the end point region, is often no hinderance to the extrapolative photometric method.

Using a photometric titrator to detect the end point in a titration which can also be performed visually increases the precision but does not necessarily increase the accuracy (23). The photometric method is amenable to automation — an advantage when routine analyses are to be performed.

The photometric method is also useful in many cases when the human eye is unable to detect the end point using a visual indicator. In general two cases can be differentiated.

First, a photometric end point is often required when strongly colored solutions are to be titrated. Interestingly, a forerunner of photometric titrations was developed to deal with such situations; in 1918, Tingle (24) applied a pocket spectroscope to the detection of end point color changes in solutions with high color backgrounds.

In the second case, a photometer can detect the color change of an indicator when that color change is "indistinct" or "dragging." A dragging end point is obtained when the titration reaction is slow or when an unfavorable equilibrium situation exists at the end point. In either case, the extrapolative photometric method is not hindered. A second possible cause of a poor visual end point lies in the subjective nature of the colors of the two forms of an indicator. A photoreceptor can differentiate easily between "colors" which appear

almost identical to the eye.

Calculation of Photometric Titration Curves

The decision as to whether or not a reaction can be used as the basis for a photometric titration can be reached by means of several calculations of varying degrees of complexity. Crude estimations can be made from an inspection of the relevant stability constants and the colors. On the other hand, it is possible to calculate the entire titration curve by using rigorously derived equations.

Titration curves for acid-base systems have been derived by Goddu and Hume (25) and by Higuchi, et al. (26).

Flaschka (27) has derived equations for both self-indicating and slope-indicating cases. The calculations are similar to those outlined in Chapter II. The results show that, with self-indicating systems, useful titrations are possible with the product $K_{MY}C_M$ as low as 50. With slope-indicating systems, the results reveal that a metal M indicated by a metal N could be titrated successfully when K_{MY}/K_{NY} was 100 or greater. These conclusions are generally in agreement with those reached in Chapter II.

Step-indicating systems have been studied theoretically by a number of workers (28-33). In essence, these studies show that a sharp step is obtained when K_{MY}/K_{MI} is greater than 10^4, K_I itself is greater than 10^4, the indicator concentration is low, and the metal concentration is high. Due to mathematical complexities, however, no completely general studies have been undertaken. The

authors have either limited the consideration to specific metal-indicator-chelon systems or have resorted to mathematical approximations. While much useful information has been obtained, the approximations used are valid only for clear cut situations and exclude the general consideration of borderline cases.

As mentioned earlier in this chapter, photometric end point detection is of greatest value when applied to borderline situations. It was therefore felt worthwhile to institute a general study and to calculate photometric titration curves for step-indicating systems under a variety of conditions. Digital computer facilities were available and were utilized to minimize the labor required for the task. The calculated curves were examined for their general properties, expecially with regard to the location of the end point.

For a metal M reacting with a complex-former Y and an indicator I, the relevant stability constants are

$$K_M = \frac{[MY]}{[M][Y]} \tag{2}$$

$$K_{MI} = \frac{[MI]}{[M][I]} \tag{3}$$

These are conditional constants but the stars (*) are omitted for simplicity. Material balances for M, Y, and I give

$$C_M = [M] + [MY] + [MI] \tag{4}$$

$$C_Y = [Y] + [MY] \tag{5}$$

$$C_I = [I] + [MI] \tag{6}$$

The fraction of M titrated, $\underline{a}$, is given by

$$a = \frac{C_Y}{C_M} \tag{7}$$

Combination of equations (2) through (7) gives the following expression for $\underline{a}$:

$$a = \frac{1}{C_M}\left[C_M - [MI] - \frac{[MI]}{K_{MI}(C_I-[MI])}\right]\left[1 + \frac{K_{MI}(C_I-[MI])}{K_M[MI]}\right] \tag{8}$$

This is a modification of the equation originally derived by Fortuin et al. (28). For simplicity in the calculation, $\underline{a}$ is again chosen as the dependent variable; in this case, the independent variable is [MI].

If MI and I are the only absorbing species, the absorbance is given by

$$\begin{aligned} A &= k[MI] + k'[I] \\ &= k[MI] + k'(C_I-[MI]) \\ &= (k-k')[MI] + k'C_I \end{aligned} \tag{9}$$

Thus, even though I absorbs, the absorbance is a linear function of [MI]. A curve calculated with MI assumed to be the only absorbing species will therefore give the general shape of the actual titration curve at any wavelength where the absorptivities of MI and I are different. The magnitude and direction of the actual absorbance change will, of course, depend on the difference in these absorptivities.

If M, Y, or MY absorbs appreciably, the absorbance is not a

simple, linear function of [MI] and the absorptivities of all absorbing species must be known in order to calculate a titration curve.

In view of these considerations, [MI] is assumed to be the only absorbing species. The absorbance is then given by

$$A = k[MI] \tag{10}$$

The value of k is arbitrary in a general calculation and is chosen for each case to be $1/C_M$ or $1/C_I$, whichever is larger, so that the domain of A is zero to one. This facilitates the comparison of different curves.

A Burroughs 220 computer was programmed to calculate, for many different numerical values of the parameters K_{MY}, K_{MI}, C_M, and C_I, the value of [MI] corresponding to each of a series of A's, $0 < A < 1$, and then the $\underline{a}$ for each [MI].

It was also of interest to study the relationship between the locations of the inflection point of the curve and the equivalence point. To that end, the second derivative of equation (8) with respect to [MI] was obtained:

$$\frac{d^2a}{d[MI]^2} = \frac{2K_{MI}^2C_IC_M(C_I-[MI])^3 - 2C_IK_M[MI]^3}{K_{MY}[MI]^3C_MK_{MI}(C_I-[MI])^3} \tag{11}$$

At the inflection point, this derivative must equal zero and therefore the numerator must equal zero. Cancelling common terms and denoting the result as D:

$$D = C_M K_{MI}^2 (C_I - [MI])^3 - K_M [MI]^3 = 0 \qquad (12)$$

Solution for [MI] in equation (12) and substitution into (7) would give an expression for the value of $\underline{a}$ at which the curve inflects. However, this procedure requires the solution of a third order polynomial. A simpler approach is the programming of the computer to also calculate the value of D associated with each [MI] and to print out this D value along with the corresponding A and $\underline{a}$. The D's can then be plotted against $\underline{a}$ and the value of $(a)_{D=0}$ determined. In fact, often no plot is necessary and the value of $(a)_{D=0}$ can be estimated by inspection or by a linear interpolation.

It would be impractical to attempt to present all of the several hundred curves obtained in this study. Only the conclusions which were drawn will be given, in conjunction with a few illustrative curves.

In Figure 6, the curve for $K_{MI} = 10^7$ is a nearly ideal step-indication titration curve. The inflection point is at $\underline{a} = 0.993$ (i.e. 0.7% low). The end point determined from the upper portion of the step is at 0.99 (1.0% low) and the end point determined from the lower portion of the step is at 1.03 (0.3% high). Thus none of the distinctive features of the curve can be used to determine the actual equivalence point. This phenomenon is generally observed in sharp step-titration curves. An end point taken at the inflection point or the second break of the curve will be nearer to the equivalence point than an end point taken at the first break. All three points move closer to the equivalence point as C_I is decreased.

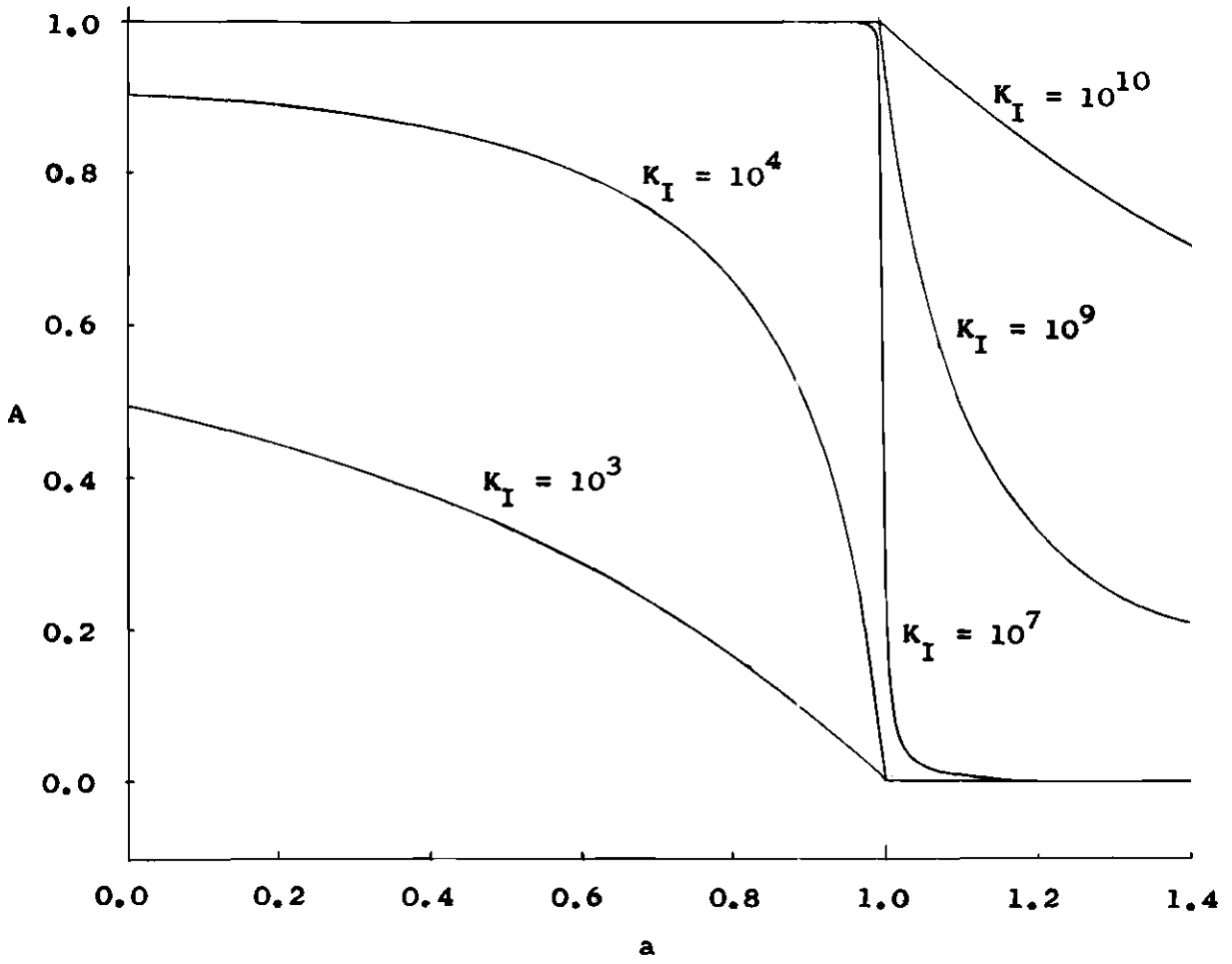

Figure 6

Influence of K_I on a Photometric Titration Curve

$K_M = 10^{10}$; $C_M = 10^{-3}$ F; $C_I = 10^{-5}$

As is also shown in Figure 6, changing the indicator constant from the value which gives a sharp, nearly symmetrical step results in rounding of one or the other end of the step. If the value of K_{MI} is lowered, the first break rounds off while the second break becomes sharper. When this rounding is considerable, only the second break can be used to determine the end point but then, fortunately, that break occurs exactly at the equivalence point. If the value of K_{MI} is increased, a break point curve is also obtained but then the first break is sharp. This first break always occurs before the equivalence point and, when sharp, is low by $10^2 C_I/C_M$ per cent. Obviously, decreasing the indicator concentration in a given titration will decrease the difference between this end point and the equivalence point.

The curves in Figure 7 illustrate the most interesting conclusion drawn from this study. These curves show the effect of increasing indicator concentration on a system which, at low C_I (the normal case), would give a break point end point. As C_I is increased, the first break becomes increasingly rounded until, ultimately, a self-indicating system is obtained. In general, whenever

$$C_I \gtrsim 10\, C_M \tag{13}$$

$$K_{MY} > 10^6 \tag{14}$$

$$K_{MI} \lesssim 10^{-1} K_{MY} C_M \tag{15}$$

the calculated photometric titration curves are those of self-indicating systems. No curvature is introduced by lowering the value

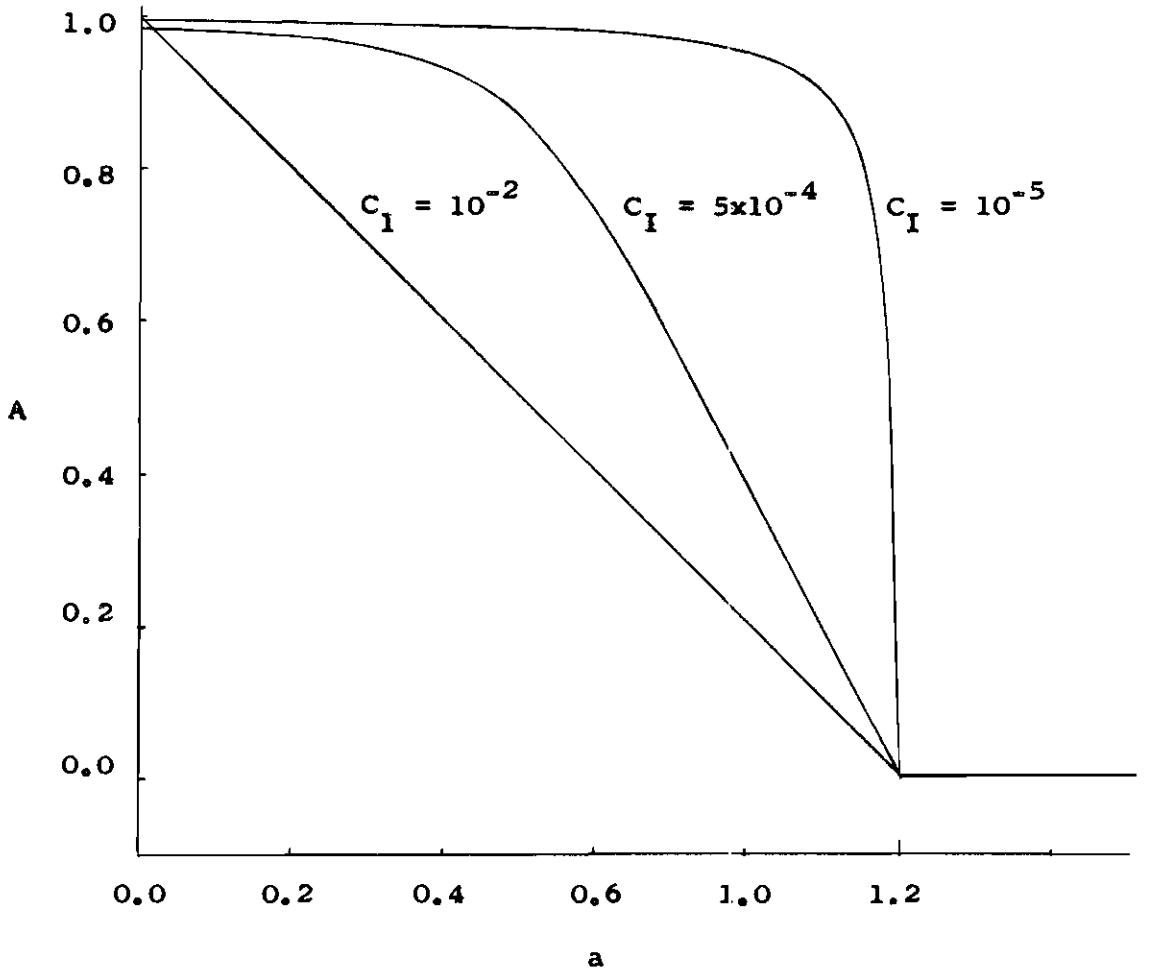

Figure 7

Influence of C_I on a Photometric Titration Curve

$K_{MY} = 10^{10}$; $C_M = 10^{-3}$ F; $K_{MI} = 10^5$

of K_{MI} so that the ultimate lower limit of that constant is fixed by the practical considerations of metal concentration, photometer sensitivity, and the magnitude of (k-k') for the dye.

Thus it is possible to create a self-indicating system by the addition of an excess of a metal indicator.* Such a self-indicating system may be used to indicate the end point in the titration of another metal (which must complex strongly with the titrant and weakly, if at all, with the indicator), thereby offering the possbility of a consecutive titration of the two metals. Such created self-indicating systems are limited to the micro and submicro ranges, however, due to the high absorptivities of most metal indicating dyes.

This study provides a theoretical background for two titration methods which have already been reported. In the first method, submicrogram amounts of calcium and magnesium were titrated with EDTA at pH 10 with the magnesium-Calmagite system providing slope-indication for calcium (21). In the second method, the zinc-Murexide system served as a slope-indicator for an EGTA titration of cadmium, also at pH 10 (34).

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* In such a case it would be preferable to use the word "dye" since "indicator" implies step-indication.

CHAPTER IV

EQUIPMENT AND CHEMICALS

Photometric Titrator

The photometric titrator used in this research was designed and built by Flaschka and Sawyer (35). With this instrument, titrations are performed with the titration vessel in the open. The design features of the instrument are discussed in some detail in Chapter X.

Several titration vessels were constructed from rectangular pieces of plate glass, bonded with epoxy glue. The stirrer was a glass rod with a small propeller at the lower end and driven by a six volt motor.

Other Instruments

Spectrophotometers

Most spectral curves were made with a Bausch and Lomb Spectronic 505 recording spectrophotometer. Screen calibrations and some spectral curves were made with a Cary Model 14 recording spectrophotometer belonging to the Coca-Cola Company whose aid is gratefully acknowledged.

pH Meter

All pH measurements were made with a Leeds and Northrup #7664 pH meter. The device was calibrated with potassium acid tartrate (saturated solution, 25^{o}C, pH 3.57).

Glassware

The usual laboratory glassware such as beakers and flasks was used as needed. All volumetric glassware was Class A and was used without additional calibration.

Chemicals

Water

Deionized water was used exclusively.

Disodium (Ethylenedinitrilo)tetraacetic Acid Dihydrate (EDTA)

J. T. Baker Chemical Company "Baker Analyzed" disodium EDTA was slurried in several hundred milliliters of water and a few pellets of sodium hydroxide were added to hasten dissolution. The solution was prepared to be approximately 0.1 F (37.2 g/l) and was standardized against a standard zinc solution.

[Ethyleneglycolbis(nitriloethyl)]tetraacetic Acid (EGTA)

Approximately 0.1 F EGTA solutions were prepared by placing 38 g of G. F. Smith Chemical Company EGTA in water, adding sodium hydroxide until dissolution was accomplished, and diluting to one liter. Turbid solutions were filtered. The EGTA solutions were also standardized against a standard zinc solution.

(Diethylenetrinitrilo)pentaacetic Acid (DTPA)

J. T. Baker Chemical Company "Baker Analyzed" DTPA was used to prepare approximately 0.1 F solutions (39.3 g/l). Sodium hydroxide was added slowly until dissolution of the DTPA was complete. The DTPA solutions were standardized against a standard zinc solution.

Xylenol Orange Indicator (XO)

Xylenol Orange indicator was kindly furnished in a very pure form by Prof. Dr. R. Pribil of Prague. Approximately 40 mg of the dye was dissolved in 10 ml of water to which a spatula tip of sodium acetate had been added.

Zincon Indicator

Zincon indicator solutions were prepared by dissolving 44 mg of the dye in 4 ml of 1 F sodium hydroxide and diluting to 10 ml. J. T. Baker Zincon was used.

Acids

DuPont concentrated nitric, hydrochloric, sulfuric, and acetic acids were used as required.

Bases

DuPont concentrated aqueous ammonia and J. T. Baker "Analyzed" sodium hydroxide pellets were used.

Zinc

Standard 0.1000 F zinc solutions were prepared by dissolving 6.538 g of Baker "Analyzed" zinc metal (99.99% pure) in the minimum amount of nitric acid. The solution was then boiled briefly to expel oxides of nitrogen, cooled, and diluted to one liter.

Cadmium

Baker "Analyzed" cadmium metal was used. Standard 0.1000 F solutions were prepared by dissolving 11.24 g of the metal in the minimum amount of nitric acid, boiling briefly, cooling, and diluting to one liter.

Other Metal Salt Solutions

J. T. Baker "Analyzed" metal salts were used to prepare the

desired solutions. In the cases of strongly acidic metal ions, acid was added to reduce hydrolysis.

Potassium Iodide

Baker U.S.P. grade potassium iodide was used. Concentrated solutions were prepared to be 100% w/v by dissolving 250 g potassium iodide in sufficient hot water to make about 240 ml, filtering, cooling, and diluting to 250 ml.

Buffer pH 5.0

Acetate buffer pH 5.0 was prepared by dissolving 68 g J. T. Baker sodium acetate trihydrate in 700 ml water, lowering the pH to 5.0 with concentrated hydrochloric acid, and diluting to one liter.

Buffer pH 6.1

Eastman hexamethylenetetraamine (140 g) was dissolved in water (700 ml), the pH was adjusted to 6.1 with 1:1 sulfuric acid, and the solution was diluted to one liter.

Buffer pH 9.40

To a solution of 54 g of J.T. Baker "Analyzed" ammonium chloride in 700 ml water, concentrated aqueous ammonia was added until a pH of 9.40 was reached. The solution was then diluted to one liter.

Other Chemicals

All other chemicals were Baker "Analyzed" reagents except that Eastman l-ascorbic acid was used.

Standardization Procedures

EDTA and DTPA Standardizations

An aliquot of the standard zinc solution was pipetted into a flask and diluted with water. This was followed by the addition of a few milliliters of buffer pH 5.0 and a drop or two of Xylenol Orange solution. The resulting solution was then titrated with an EDTA or DTPA solution until the indicator color changed from red to yellow.

EGTA Standardization

An aliquot of standard zinc solution was pipetted into a phototitrator cell and diluted with water. Then a few milliliters of buffer pH 9.4 and several drops of Zincon solution were added. The resulting solution was then titrated photometrically with EGTA solution at 622 nm.

Storage of Solutions

All chelon and indicator solutions, all alkaline solutions, and all dilute (0.001 F or less) metal ion solutions were stored in polyethylene bottles.

CHAPTER V

TITRIMETRIC ANALYSES FOR CADMIUM AND ZINC

The titrimetric determination of cadmium in the presence of zinc or vice versa has long been an analytical problem. The two metals are strikingly similar in their chemical behavior and only a few selective reactions are known. The ferrocyanide titration of zinc has been widely applied but must be considered unsatisfactory because of the nonstoichiometric and variable composition of the product of the titration reaction; also, only limited amounts of cadmium can be tolerated (36). The remaining titrimetric methods which have been reported require a prior separation of cadmium and zinc. When one metal is present in the sample in great excess of the other, the separation is especially difficult. The classical sulfide precipitation of cadmium, for instance, is complicated by coprecipitation and postprecipitation and several reprecipitation steps are often required to effect a complete separation from zinc. Several ion exchange separations of cadmium and zinc have been reported, e.g. (38), but these, like precipitation methods, are highly time consuming. Electrolytic separations and determinations are possible but are often tedious and generally require complex and expensive equipment (36,37).

Instrumental methods are available for some cadmium and zinc determinations. For instance, when present in approximately equal

amounts, both can be determined polarographically in the presence of many other ions if the usual error in the method (up to about five per cent) can be tolerated (39). Since, under most conditions, the polarographic half-wave potential of cadmium is about 0.6 volts more positive than that of zinc, cadmium can readily be determined polarographically in the presence of very large amounts of zinc (40,41,42). Obviously, the converse is not possible. AC and other modified polarographic methods are useful in the analysis of trace quantities of zinc, even in the presence of rather large amounts of cadmium (36). Unfortunately, the expense of the complicated equipment required for these methods constitutes a severe limitation on their usefulness.

The introduction of chelons and the application of instrumental end points have offered new possibiliteis for selective titrations of cadmium and zinc. Sweetser and Bricker (43) have developed an EDTA titration of cadmium in the presence of zinc using a photometric end point (236 nm). Selectivity is achieved by titrating in strongly alkaline medium so that zinc is present as the unreactive zincate. A small amount of cyanide is added to prevent the precipitation of cadmium hydroxide. The ultraviolet absorbance of uncomplexed, anionic EDTA is followed to determine the end point. The requirement for an ultraviolet photometric titrator, the high alkalinity, and the fact that the cyanide concentration is critical are disadvantages of the method.

Other workers have attacked the cadmium-zinc problem via application of more selective titrants and use of auxiliary com-

plexing agents. EGTA differs from other chelons in that the absolute stability constant of the Cd-EGTA complex is significantly greater (by about four log units) than the constant of the Zn-EGTA complex. Further, zinc forms more stable ammonia complexes than does cadmium; thus in an ammoniacal medium there is an increase in the difference of the effective stabilities of the cadmium and zinc chelonates.

Flaschka and Speights (44) have applied EGTA to an amperometric titration of cadmium in the presence of zinc. The diffusion current of cadmium is followed at -0.90 or -0.70 volts vs. S.C.E. in ammonia or acetate buffered medium, respectively. Further, in a medium of appropriate ammonia concentration, the effective stability constant of copper-EGTA falls between the cadmium and zinc constants and copper can be used as an amperometric indicator for cadmium at -0.30 volts vs. S.C.E. Successful titrations of cadmium were achieved with the Zn:Cd ratio as high as 500.

Flaschka and Ganchoff (45) have utilized EGTA for a photometric titration of cadmium in the presence of zinc. In ammoniacal medium buffered at pH 10, copper serves as a slope indicator for cadmium. Zinc, when present in large amounts, degrades the copper end point but does not affect either the location or the quality of the cadmium end point. Zn:Cd mole ratios of up to 500:1 could be tolerated.

Fabregas, et al. (46) have developed a method for the determination of zinc in the presence of cadmium, utilizing the differences in the stability constants of the EGTA complexes of cadmium, zinc, and lead. When lead-EGTA is added to a solution

containing zinc, cadmium, and sulfate, only the cadmium is capable of replacing lead from its EGTA complex. The lead thus replaced precipitates as the sulfate and is filtered off. Zinc is then titrated in the filtrate. The maximum Cd:Zn mole ratio which can be tolerated is about 10:1; at higher ratios, the zinc determination is unsuccessful.

It is, of course, possible to determine both cadmium and zinc chelometrically with the aid of one of the above methods. At first, the sum of cadmium and zinc is determined by one of several available methods. Then one (preferably the minor) constituent is determined by one of the procedures just described. The difference in the results of these two determinations gives the other component. Recently, however, two methods have been proposed which allow the determination of both cadmium and zinc in a single titration.

Aikens et al. (47) have developed a photometric titration for cadmium and zinc which can be applied when the Cd:Zn ratio is between about 0.1 and 10. DTPA is the titrant and copper is added as a slope-indicator at 700 nm. In 0.5 F ammonia buffer pH 10, the stability constants of Cu-DTPA and Zn-DTPA are quite close together and about three log units less than the Cd-DTPA constant. Under these conditions, a three part titration curve is obtained: The initial, horizontal portion of the curve corresponds to the titration of cadmium; in the second, rising, section copper and zinc are cotitrated; after the second end point, the curve is again horizontal. The quality of both end points is poor and strongly dependent on the Cu:Zn ratio. Further, the zinc result is obtained by

subtraction of the added amount of copper from the result for copper plus zinc and is subject to the loss of significant figures which occurs when two numbers of similar magnitudes are subtracted.

Flaschka and Carley (34) have developed a method for the consecutive microtitration of cadmium and zinc. EGTA is the titrant and the zinc-Murexide complex serves as a slope-indicator for cadmium. The titration is performed at pH 10 in a solution which is 0.02-0.03 F in total ammonia.

CHAPTER VI

THE CONSECUTIVE PHOTOMETRIC TITRATION OF CADMIUM AND ZINC

Introduction

The method, mentioned in Chapter V, for the consecutive titration of cadmium and zinc (34) is hampered by the fairly rapid decomposition of Murexide in aqueous solutions. A search was therefore instituted in order to find a more suitable indicator for the titration and Zincon was found to be satisfactory. Zincon fulfills the requirements for the method; i.e. it combines only weakly with cadmium and forms a strongly colored zinc complex from which the zinc is readily removed by EGTA. Further, Zincon is more stable in solution than Murexide and shows no detectable decomposition for several hours (48). In addition, the color reaction of zinc with Zincon is somewhat more sensitive than with Murexide so that smaller amounts of zinc or more dilute solutions could be titrated if the former dye were used. The proposed method should, therefore, be an improvement over the Murexide method. Finally, the absorbance maximum of the Zinc-zincon complex is at 625 nm while, with Murexide, the titration is performed at 456 nm; thus a procedure using Zincon as the indicator would complement the Murexide method for use with samples which contain colored impurities absorbing strongly at the Murexide wavelength.

Experimental

All titrations were performed with the phototitrator described in Chapter IV using a two cm titration vessel of 200 ml capacity. All of the reagents required for the experiments described in this section were prepared and standardized according to the procedures given in Chapter IV.

Preliminary Investigations

The absorbance curves of Zincon and its zinc and cadmium complexes are shown in Figure 8. The maximum difference between the free Zincon and Zn-Zincon curves occurs at about 625 nm and highest sensitivity will be obtained when the titration is performed at that wavelength. An interference filter with a nominal wavelength of 622 nm was available and was employed in all investigations.

At 625 nm, the maximum color sensitivity of the zinc-Zincon complex occurs at pH 8.5-9.5. In this pH range, the sensitivity is approximately constant, falling off sharply at both ends of the plateau. In the presence of excess Zincon, a series of preliminary titrations of zinc with EGTA indicated that the titration reaction is somewhat slow, the rate increasing with increasing pH. A pH of 9.4 was selected for the titration in order to obtain the maximum reaction rate without approaching too closely the pH at which sensitivity begins to decrease.

At pH 9.4 and in the presence of excess Zincon, several titrations showed the reaction of cadmium with EGTA to be slow. The rate increases with the amount of ammonia buffer present but, at the

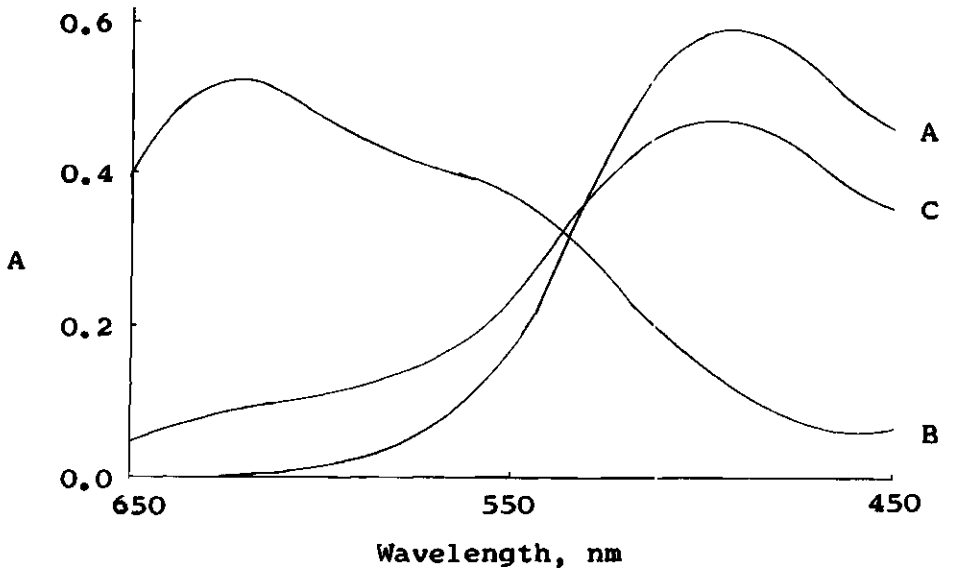

Figure 8

Spectral Curves of Zincon and Its Cadmium and Zinc Complexes

pH 9.4

C_{NH_3} = 0.03 F

A. Free Zincon
B. Zn-Zincon
C. Cd-Zincon

higher ammonia concentrations, the color intensity of the Zn-Zincon complex is decreased so that the sensitivity is reduced. At the pH selected, 0.01-0.03 F total ammonia was found to be the optimum for the titration.

It is known that the addition of organic solvents often enhances the rates of slow exchange reactions involving indicators (49). The effects of organic solvents on the present reaction were therefore investigated. Addition of acetone or n-propanol to the titration solution resulted in little effect but it was found that the reaction rate increased noticably when the titration solution contained 20 per cent ethanol.

Another series of titrations for cadmium and zinc with EGTA was performed in order to assess the influence of the Zincon concentration. At the pH and ammonia concentration selected, it was found that a Zincon concentration of about 0.06 mg/ml in the titration solution was the most satisfactory. Higher Zincon concentrations resulted in excessive rounding in the end point regions of the titration curve while lower concentrations resulted in unsatisfactorily slow reaction rates, even in the presence of ethanol.

Since many metal ions give stronger EGTA complexes than cadmium and zinc, the selectivity of the proposed method is not expected to be high. Separation of cadmium plus zinc is possible by several methods (e.g. ion exchange, solvent extraction, controlled potential electrolysis) so that the method might find application after such a separation has been effected. Calcium, however, was studied as a possible interference in this submilligram technique

because of its almost universal presence in water and reagents.

Small amounts of calcium appear to be cotitrated with cadmium. A pretitration procedure was therefore applied to correct for any calcium in water and/or reagents. The pretitration cannot correct for calcium in the sample solution, however.

Procedure

Into the titration vessel, place 5 ml of 1 F ammonia buffer pH 9.4, 2 ml of 4.4 mg/ml Zincon solution, 30 ml of ethanol, and water to make about 140 ml. Adjust the instrument to obtain a transmittance reading of about 90 per cent, add small (but not necessarily known) amounts of cadmium and zinc, and titrate with 10^{-3} F EGTA. Readjust the instrument, if necessary, so that about 90 percent transmittance is again indicated, add the sample solution, and complete the titration with the same titrant.

Results and Discussion

The titration curve obtained is treated as shown in Figure 9. Some results for the titration of cadmium and zinc using the pretitration technique are presented in Table 1. The titration reaction is somewhat slow during the titration of cadmium. This is not highly objectionable, however, since only a few points are needed to establish each straight portion of the curve. No points are required near the cadmium end point where the reaction is slowest; the necessity of waiting a few seconds for each of the several points on the cadmium portion is not a great hinderance. It should be noted, with reference to Figure 9, that the total of the cadmium and zinc

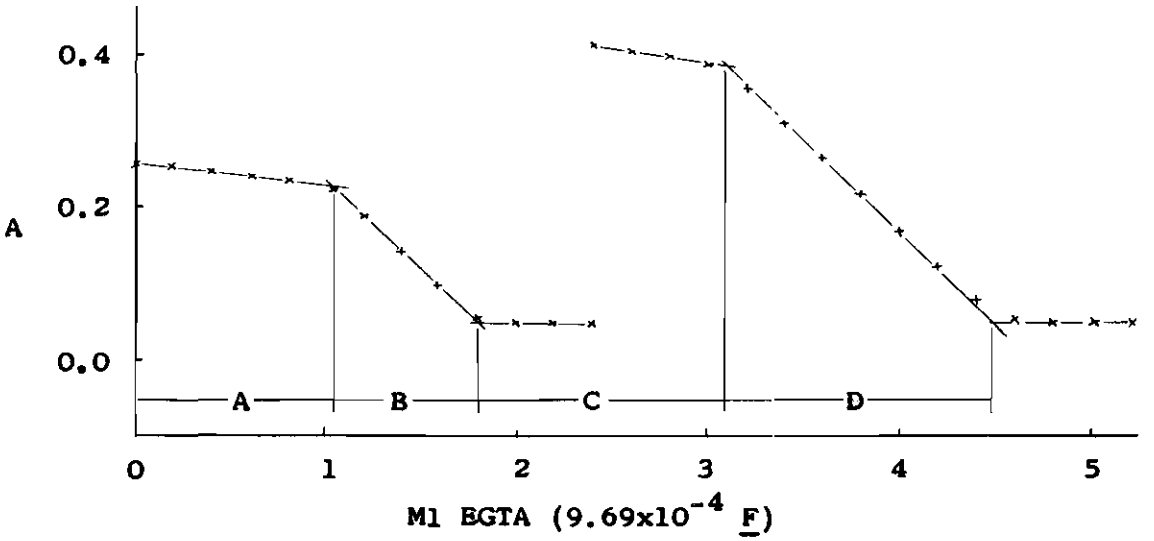

Figure 9

Determination of Cadmium and Zinc
Using the Pretitration Method

Cd ≙ B + C; Zn ≙ D - B

Table 1

Results of titrations of Cadmium and Zinc by the Pretitration Method

µg Cd Taken	M1 9.69×10^{-4} F EGTA			µg Zn Taken	M1 9.69×10^{-4} F EGTA		
	Calc.	Found	Diff.		Calc.	Found	Diff.
222	2.04	2.04	0.00	38.0	0.60	0.58	-0.02
169	1.55	1.74	+0.19	146	2.31	2.19	-0.12
184	1.69	1.69	0.00	21.1	0.33	0.32	-0.01
168	1.54	1.59	+0.05	66.0	1.04	0.99	-0.05
498	4.57	4.62	+0.05	19.6	0.31	0.34	+0.03
400	3.67	3.66	-0.01	34.7	0.55	0.55	0.00

added for the pre-titration must be somewhat less than equivalent to the amount of cadmium present in the sample.

Further Investigations

Several titrations were performed to assess the influence of larger amounts of calcium. When the calcium present was equivalent to about 10 per cent the cadmium anomalities were observed in the titration curve just before the cadmium end point and inconsistent results were obtained. Addition of an amount of calcium approximately equivalent to the cadmium resulted in a titration curve of the type shown in Figure 10. The middle segment of the curve corresponds to calcium; due to the very low stability of the Ca-Zincon complex, this segment is nearly horizontal. The angle of intersection between the calcium and zinc portions of the curve is superior to the angle between the portions corresponding to cadmium and zinc segments when no calcium is present. The angle between the portions corresponding to cadmium and calcium is inferior but can be improved by increasing the Zincon concentration and, thereby, the slope of the cadmium segment. With increasing dye concentration, however, the curvature at the zinc end point increases, requiring that the titration be carried far beyond that point in order to establish the final, horizontal portion of the curve. In order to determine the absorbance level of the horizontal, it is convenient to add a drop of rather concentrated titrant (e.g. 0.1 *F*) after the zinc segment of the curve begins to level off. When calcium is deliberately added to the sample, the pretitration is not necessary and, indeed,

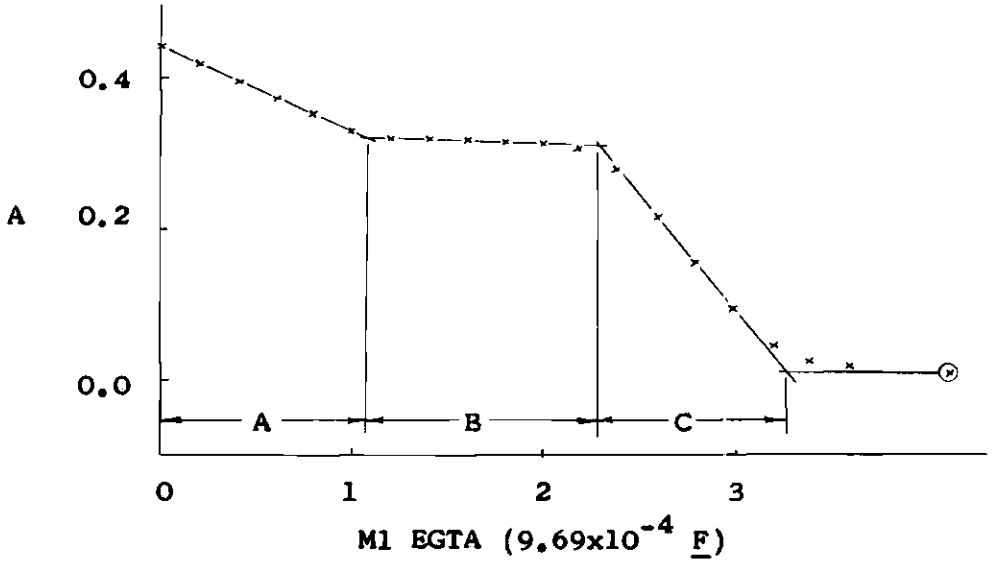

Figure 10

Determination of Cadmium and Zinc
After the Addition of Calcium

Cd ≙ A; Ca ≙ B; Zn ≙ C

The circled point is the absorbance obtained after the addition of one drop of 0.1 F EGTA and is plotted, for convenience, at 3.8 ml.

is impossible if the dye concentration is increased in order to improve the first end point.

Procedure

Into the titration vessel, place 5 ml of 1 F ammonia buffer pH 9.4, 6 ml of 4.4 mg/ml Zincon solution, 30 ml of ethanol, and water to make about 140 ml. Adjust the instrument to obtain a transmittance reading of about 90 per cent. Add the sample and an amount of calcium approximately equivalent to the cadmium and titrate in the usual manner with 10^{-3} F EGTA, obtaining several points on each but the last straight portion of the curve. After the curve begins to level off near the zinc end point, add one or two drops of 0.1 F EGTA and read the absorbance corresponding to the last, horizontal segment of the curve.

Results and Discussion

The results of several titrations in which calcium was deliberately added to the cadmium-zinc sample are presented in Table 2.

The titration reaction is again somewhat slow, not only on the cadmium portion of the curve, but also on the calcium portion. As before, however, only a few points are needed on each section of the curve and the waiting time is not excessive. The accuracy and precision of the method are adequate.

The titration of cadmium and zinc in solutions to which calcium has been deliberately added has several advantages. The pre-titration is eliminated so the time required for a titration is

Table 2

Results of Titrations of Cadmium and Zinc

After the Addition of Calcium

µg Cd Taken	Ml 9.69×10^{-4} F EGTA			µg Zn Taken	Ml 9.69×10^{-4} F EGTA		
	Calc.	Found	Diff.		Calc.	Found	Diff.
111	1.02	1.03	+0.01	32.7	0.51	0.50	-0.01
111	1.02	0.93	-0.09	65.4	1.03	1.02	-0.01
111	1.02	1.06	+0.04	65.4	1.03	1.00	-0.03
111	1.02	1.02	0.00	65.4	1.03	0.97	-0.06
223	2.04	2.08	+0.04	65.4	1.03	1.00	-0.03
223	2.04	2.08	+0.04	65.4	1.03	0.99	-0.04
1113	10.21	10.10	-0.11	65.4	1.03	1.05	+0.02
1113	10.21	10.07	-0.14	65.4	1.03	1.05	+0.02

considerably shortened. Each result is computed from two experimental values rather than four and thus is less subject to experimental error. Further, the angles at the cadmium and calcium end points are both superior to the cadmium end point angle in the pre-titration method. Lastly, any calcium in the sample solution, as well as in the water and reagents, is corrected for.

This method is unique in that it allows the separate determinations of three metals from a single titration curve. It is unlikely that an application requiring the submilligram determination of calcium as well as cadmium and zinc will arise; calcium is seldom found in conjunction with the other two metals, especially following a separation of cadmium plus zinc. The feasibility of such a triple determination has been clearly demonstrated, however, and the advantages of the conversion to a slope-indicating system have again been emphasized. It is certainly possible that consecutive titration procedures will be developed for other, more interesting, three metal systems.

CHAPTER VII

THE EDTA TITRATION OF ZINC IN THE PRESENCE OF CADMIUM

Introduction

As noted in the preceding chapter, several titrimetric methods are now available for the determination of cadmium in the presence of zinc. Submilligram amounts of both metals can also be determined if the cadmium:zinc ratio lies between about 0.1 and 10. However, no satisfactory titrimetric methods have been reported for the determination of macro quantities of cadmium and zinc in the same sample or for the determination of zinc in the presence of great amounts of cadmium.

It was thought worthwhile to attempt the development of a selective method for the titration of zinc. At first, an investigation was initiated to seek a reagent which is capable of masking cadmium against reaction with chelons but which does not hinder the titration of zinc. A number of chemicals which are known to form more stable complexes with cadmium than with zinc were investigated without success. One day, an accidentally large amount (several grams) of potassium iodide was added to a few milliliters of a weakly acidic test solution containing cadmium and the metallochromic indicator Xylenol Orange. Iodide, in moderate concentrations had been investigated earlier but had shown no effect. This time, amazingly, the red color of the cadmium-Xylenol Orange

complex was supplanted by the yellow color of the free indicator. Further experiments showed that iodide is capable of removing cadmium from a number of indicator complexes either partly or completely, depending on the indicator, pH, and iodide concentration. Under the same conditions, in contrast, the corresponding zinc-indicator complexes are affected only slightly or not at all. These findings offered the possibility that iodide might also be capable of masking cadmium from reaction with chelons. A preliminary series of EDTA titrations of known amounts of zinc in the presence of cadmium indicated that iodide indeed is capable of masking cadmium without impairing the titration of zinc.

Ligands which form highly stable complexes are generally preferred for the masking of interferences in chelometric titrations. Thus, 1:1 complexes, whose stabilities are enhanced by the chelate effect, or 1:n complexes of exceptionally high stability are commonly employed. Usually, only moderate concentrations of such ligands are required. There are only a few cases in which masking has been achieved by the use of high concentrations of ligands which form relatively weak complexes with the metal(s) to be masked. Notable examples are the sulfate masking of thorium* (50) and, recently, the masking of bismuth by ammonium chloride in nearly saturated solutions** (51). To be effective, masking agents which form complexes of low stability must be present in very high concentrations. Theoretical predictions of the effectiveness of such masking are

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* $\log K_{Th(SO_4)_2} = 5.6$ (10)

** $\log K_{Bi(Cl)_6} = 6.6$ (10)

almost impossible since the relevant stability constants, when known, are applicable only in media of low ionic strength (ca. 0.1). In order to emphasize the special features of this type of masking, the name "low stability masking" has been proposed (52).

Several investigations were undertaken in order to find the optimum conditions for the titration of zinc with iodide masking of cadmium. Xylenol Orange had already been shown to be a satisfactory indicator for the titration. Several other dyes were studied but none proved superior to Xylenol Orange.

In solutions of low ionic strength, the bright yellow color of uncomplexed Xylenol Orange persists up to pH about six; above that pH, the indicator is red. In a 50 per cent (w/v) solution of potassium iodide, however, the dye shows an obvious reddening at about pH 5.5, probably because of an ionic strength effect. Thus it is necessary to perform the zinc titration at a pH somewhat below 5.5. However, at a pH lower than about 4.5, the conditional stability constant of the zinc-indicator complex is so low that the titration of zinc to a Xylenol Orange end point is impossible. It was therefore necessary that the proposed titration be performed at a pH somewhere between 4.5 and 5.5. Experiments showed that sharp end points and good results could be obtained near pH 5.0 and that pH was chosen for the titration. Other experiments revealed that the indicator concentration is not critical and can be varied to suit the individual. The procedure which resulted from these investigations is given below.

Reagents

The reagents used were prepared and standardized according to the procedures described in Chapter IV.

Procedure

Place 15 ml pH 5 acetate buffer, 30-50 g potassium iodide and a small crystal of sodium thiosulfate* in the titration vessel. Add a sample solution containing about two milligrams zinc and up to about one gram cadmium. Add 4-5 drops of a 4 mg/ml Xylenol Orange solution, dilute the resulting solution to about 100 ml, and titrate with 0.01 F EDTA.

Results and Discussion

The results of several titrations of zinc, alone and in the presence of cadmium and some other metals, are presented in Table 3. These and some additional data have been subjected to a statistical treatment. The standard deviation for the titration of zinc alone was 0.018 ml and for the titration in the presence of cadmium, 0.024 ml.

Potassium iodide may be added to the titration solution either as the solid or as a concentrated solution (e.g. 60 per cent w/v), the addition of the solid being decidedly more convenient. The cooling resulting from the dissolution of potassium iodide does not perceptible affect the quality or location of the end point. The amount of potassium iodide required for effective masking of

---

* Thiosulfate is added to reduce any free iodine, traces of which may be present in the potassium iodide or may be produced by air oxidation of iodide in the solution.

cadmium seems not to depend on the cadmium:zinc ratio but rather on the cadmium concentration. For up to about 200 mg cadmium per 100 ml solution, a concentration of 30 per cent w/v potassium iodide is sufficient; for larger amounts of cadmium (up to about 1 g per 100 ml) 50 per cent is necessary.

The method can be applied on the macro scale but restriction to the micro range is desirable for economic reasons.

With increasing amounts of cadmium present, the color change at the end point is no longer to the canary yellow of free Xylenol Orange but more and more to a dull yellow with a reddish tint. The initial weakening of the red of the Zn-Xylenol Orange complex spreads over several drops of titrant but the disappearance of the last of the deep red is sharp and within a fraction of a drop. Unless, due to very high cadmium concentrations, this initial dragging is extremely pronounced, it is no obstacle and the end point can be readily perceived. The addition of a few drops of EDTA more than equivalent to the zinc present produces no observable color change; the bright yellow of the free Xylenol Orange can usually be obtained only by the addition of considerable amounts of EDTA (up to several milliliters) after the end point has been reached.

One might attempt to predict the effects of various metal ions on the titration, knowing the stability constants of the corresponding metal-EDTA, -Xylenol Orange, and -iodo complexes. However, even qualitative predictions will often be in error because of the uncertainty due to the high ionic strength of the medium. The known concentration constants cannot be applied rigorously

because of the large, unknown effect of the high ionic strength on activity coefficients. Thus one can only offer an educated guess as to which metals will interfere and which will not. The question must, of course, be settled empirically.

For example, calcium and magnesium do not interfere with the titration of zinc at pH 5 when no iodide is present; under the present conditions, however, both calcium and magnesium do interfere. Calcium is important because it is often found in zinc-bearing minerals and as an impurity in water and reagents. Magnesium is commonly found in alloys with cadmium and zinc. Closer investigation of the calcium and magnesium interferences revealed that, fortunately, those metals can be tolerated up to about 4:1 and 10:1 mole ratios to zinc, respectively. These tolerances exclude any interference by trace contaminants and, in addition, offer the possibility of determining zinc after only a rough separation from magnesium.

When the ratios of calcium and magnesium to zinc are somewhat higher than those mentioned above, the color change at the end point is sluggish. With much higher ratios, the end point cannot be located at all. It is interesting to note that, when the sluggish end point can be located, it clearly falls short of the equivalence point. A similar phenomenon was reported in another system by MacNevin and Kriege (53): In a titration of palladium, results low by as much as 50 per cent were obtained when rhodium was present. It is not certain that the cause is the same in both cases because no explanation is available for either.

Some other elements which frequently appear in conjunction with zinc in alloys and other materials were studied as possible interferences. Lead is masked by iodide and does not interfere if the lead:zinc ratio is less than 25. A twofold excess of copper over zinc is permissible; the iodine formed by the reaction of copper(II) with iodide is reduced with thiosulfate. Aluminum blocks the indicator. This last interference is especially unfortunate as zinc is often used with aluminum in alloys; a rapid electrolytic separation of zinc from aluminum is possible, however. Iron(III) also blocks the indicator. If the iron(III) is reduced with ascorbic acid, the iron(II) formed is cotitrated with the zinc. Numerous other metal ions shown to interfere include bismuth, chromium, cobalt, and nickel.

Cadmium and zinc can be separated from many other metals by electrodeposition at a mercury cathode. Then the mercury can be distilled off and the residue analyzed, or the amalgam can be dissolved in acid. Both of these possibilities are time consuming and the latter requires the waste of much expensive mercury. It is clearly preferable to return the metals to a solution by anodic stripping of the amalgam but, unless a controlled potential source is available, some mercury will also be dissolved. This last possibility would offer a useful method if mercury did not interfere in the present procedure. The prospects were good because iodide is known to mask mercury from reaction with EDTA (54); this, it should be noted, is not a case of low stability masking since log K_{HgI_4} = 29.8 (10). An experiment showed that mercury is indeed masked in

the present method. A mercury-zinc ratio of 100:1 was easily tolerated and higher ratios should also be tolerable.

Table 3

Results of Titrations of Zinc, Alone and in the Presence of Some Other Metal Ions

Mg Zn Taken	Ml. 8.932×10^{-3} F EDTA Calc.	Found	Diff.	% KI w/v	Metal Added (mg)	Mole Ratio X:Zn
0.654	1.12	1.14	+0.02	30		
0.981	1.68	1.70	+0.02	30		
1.31	2.24	2.26	+0.02	30		
1.57	2.69	2.69	0.00	30		
1.70	2.91	2.92	+0.01	30		
1.96	3.36	3.37	+0.01	30		
1.96	3.36	3.38	+0.02	60		
2.16	3.70	3.73	+0.03	30		
2.49	4.26	4.28	+0.02	30		
2.62	4.48	4.50	+0.02	0		
2.62	4.48	4.48	0.00	15		
2.68	4.59	4.61	+0.02	30		
16.34	27.99	27.98	-0.01	0		
16.34	27.99	28.00	+0.01	0		
2.62	4.48	4.49	+0.01	6	Cd (5)	1
2.62	4.48	4.49	+0.01	15	Cd (45)	10
2.62	4.48	4.48	0.00	25	Cd (110)	25
2.75	4.70	4.73	+0.03	30	Cd (170)	36
2.55	4.37	4.37	0.00	30	Cd (170)	38
2.16	3.70	3.72	+0.02	30	Cd (170)	45
2.62	4.48	4.47	-0.01	30	Cd (220)	50
1.64	2.80	2.83	+0.03	30	Cd (170)	60
1.31	2.24	2.27	+0.03	30	Cd (170)	75
0.981	1.68	1.71	+0.03	30	Cd (170)	100
2.62	4.48	4.47	-0.01	50	Cd (450)	100
0.850	1.46	1.50	+0.04	30	Cd (170)	120
0.654	1.12	1.15	+0.03	30	Cd (170)	150
0.327	0.56	0.56	0.00	30	Cd (170)	300
2.62	4.48	4.46	-0.02	50	Cd (1300)	300 (a)
2.62	4.48	4.47	-0.01	50	Pb (210)	25 (b)
2.62	4.48	4.52	+0.04	30	Cu (6)	2.5 (c)
1.96	3.36	3.36	0.00	30	Mg (7)	10
2.62	4.48	4.46	-0.02	30	Ca (6)	4
2.62	4.48	4.47	-0.01	30	Hg (800)	100 (d)

(a) End point poor.
(b) End point slow, going to a dull yellow.
(c) Iodine removed with thiosulfate; end point dragging to a dull yellow.
(d) End point slightly sluggish.

CHAPTER VIII

THE PHOTOMETRIC TITRATION OF ZINC IN THE PRESENCE OF CADMIUM

Introduction

In the preceding chapter, a visual method for the EDTA titration of zinc was reported. Cadmium and several other metals were masked with large quantities of iodide and Xylenol Orange served as the indicator. The application of the method is limited, however, in that only small amounts of calcium and magnesium can be tolerated and that the deterioration of the end point with increasing cadmium concentration sets the maximum cadmium:zinc ratio at about 300. A photometric method can often be applied to systems which do not allow visual detection of the end point; in the present case, it should allow titration over a more extended range than the visual method. The photometric technique was therefore applied to the zinc titration.

In order to select a wavelength for the titration, the spectral curves of free Xylenol Orange and its zinc complex were obtained. These curves are presented in Figure 11. The absorbance curve of Cadmium-Xylenol Orange in the absence of potassium iodide is also shown; in solutions containing 10 or more per cent potassium iodide, the complex dissociates almost completely. The maximum absorbance difference between the zinc-Xylenol Orange complex and the free indicator occurs at about 572 nm and, in order to attain maximum sensitivity, that wavelength is preferred for the titration. An

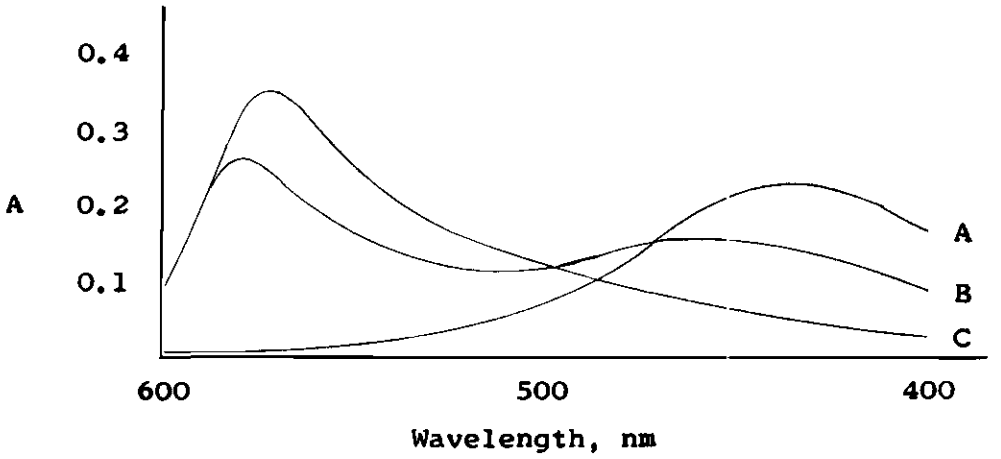

Figure 11

Spectral Curves of Xylenol Orange and
Its Cadmium and Zinc Complexes at pH 5

A. XO
B. Cd-XO
C. Zn-XO

interference filter with a nominal wavelength of 568 nm was available and was employed throughout the investigation.

Some preliminary investigations indicated that, in concentrated potassium iodide solutions, zinc could be successfully titrated with EDTA to a photometric end point in the presence of up to about a 3000-fold molar excess of cadmium. However, when the cadmium:zinc mole ratio was more than a few hundred, prolonged drift of the galvanometer after each addition of titrant implied that the titration reaction was quite slow. Neither the addition of ethanol nor the changing of the concentrations of buffer, indicator, or iodide improved the situation. Other chelons were therefore investigated as titrants and DTPA was found to be satisfactory. With DTPA as the titrant, the titration reaction is fast except near the end point; there, however, because of the extrapolative nature of the method, no data are needed. It also proved possible to titrate zinc in the presence of large excesses of cadmium despite the fact that the DTPA complex of cadmium is somewhat more stable that that of zinc [log K_{CdY} = 19.0, log K_{ZnY} = 18.0 (10)]. The situation with DTPA was expected to be less favorable than with EDTA [log K_{CdY} = log K_{ZnY} = 16.5 (10)] although, of course, no firm predictions could be made because of the effect of the high ionic strength.

With the feasibility of the DTPA titration of zinc demonstrated, optimum pH and indicator concentration were sought. Below pH 5.0, it was found that the degree of dissociation of the zinc-Xylenol Orange increases rapidly with decreasing pH. This, of course, decreases the sensitivity of the method. Only slightly

above pH 5.0, the rate of the titration reaction slows considerably and, in high concentrations of potassium iodide, the indicator begins to change to its red form, having an absorbance maximum near 570 nm. A pH of 5.0 was therefore selected for the titration. A Xylenol Orange concentration of about 0.01 mg/ml in the titration solution was found to be satisfactory.

Reagents and Apparatus

The reagents were prepared and standardized as described in Chapter IV. The photometric titrator described in Chapter IV was employed in conjunction with an interference filter with a nominal wavelength of 568 nm. All titrations were performed in a rectangular glass cell of two centimeters light path and 60 milliliters capacity.

Procedure

Place a sample solution containing 100-250 micrograms zinc and up to about 0.5 g cadmium in the titration vessel and neutralize if necessary. Add about five ml acetate buffer pH 5.0 and 10-25 ml of 100 per cent w/v potassium iodide solution. Dilute the resulting solution to about 40 ml, place the cell in the photo-titrator, and adjust the latter to indicate a transmittance of 105-110 per cent. Add two drops of 4 mg/ml Xylenol Orange solution and titrate in the usual manner with standard 10^{-3} F DTPA.

Results and Discussion

The results of several titrations of zinc, alone and in the

presence of some other metals are presented in Table 4. The standard deviation for the titration of zinc alone is 0.02 ml and, in the presence of cadmium, 0.04 ml.

With increasing amounts of cadmium present, the titration curve degenerates as indicated in Figure 12. The tendency toward positive errors with increasing amounts of cadmium may be due to the nature of the end point or to the presence of small amounts of impurities, probably zinc, in the cadmium.

The results of this investigation provide a further example of one of the advantages of photometric titrations: Solutions with a cadmium:zinc ratio of 3300 were successfully titrated in contrast to the visual method in which the maximum ratio was about 300. The titration curves in Figure 12 indicate the unfavorable equilibrium at the end point which renders the visual method impossible at fairly low cadmium:zinc ratios.

With the photometric end point, the situation with regard to other interferences also improves considerably. Calcium can be tolerated in greater than a 600-fold molar excess. Magnesium was tested up to a 3000-fold excess and even greater amounts should not interfere. Lead does not interfere if the mole ratio to zinc is less than about 600. Mercury is again masked by iodide and does not interfere when present in any reasonable amount. A copper:zinc mole ratio of 200 can be tolerated. Aluminum, if masked by Tiron, can be present in about a 20-fold excess; chromium and bismuth can be tolerated to about the same extent. The addition of tartrate (ca. 0.05 F) does not result in an interference but does not materially

Table 4

Results of Photometric Titrations of Zinc,
Alone and in the Presence of Other Metal Ions

µg Zn Taken	Ml 1.014×10^{-3} F DTPA Calc.	Found	Diff.	Metal Added	Mg	Mole Ratio Metal:Zn	% KI w/v	
131	1.97	1.97	0.00				30	
131	1.97	1.95	-0.02				30	
131	1.97	1.97	0.00				63	
229	3.45	3.47	+0.02				30	
262	3.94	3.95	+0.01				30	
262	3.94	3.98	+0.04				63	
248	3.81	3.82	+0.01	Cd	282	660	63	
98	1.48	1.48	0.00	Cd	169	1000	63	
262	3.94	3.90	-0.04	Cd	450	1000	63	
163	2.47	2.53	+0.06	Cd	280	1000	50	(a)
248	3.81	3.84	+0.03	Cd	564	1320	63	
131	1.97	2.00	+0.03	Cd	337	1500	50	
131	1.97	2.02	+0.05	Cd	450	2000	63	
131	1.97	2.00	+0.03	Cd	562	2500	63	
98	1.48	1.52	+0.04	Cd	562	3300	63	
163	2.47	2.47	0.00	Mg	122	3000	50	
163	2.47	2.47	0.00	Ca	20	200	50	
98	1.48	1.49	+0.01	Ca	40	670	50	
196	2.96	3.00	+0.04	Pb	124	200	50	
105	1.58	1.61	+0.03	Pb	207	630	50	
98	1.48	1.46	-0.02	Bi	0.4	1	50	
229	3.45	3.52	+0.07	Bi	4	6	50	
131	1.97	2.01	+0.04	Bi	6	10	50	
163	2.47	2.47	0.00	Cu(II)	32	200	50	(b)
196	2.96	2.98	+0.02	Cr(III)	3	20	50	
131	1.97	1.97	0.00	Hg(II)	320	800	50	
203	3.06	3.07	+0.01	Al	0.3	3	50	(c)
235	3.55	3.57	+0.02	Al	0.3	3	50	(d)
163	2.47	2.45	-0.02	Al	1	20	50	(d)

(a) Solution 0.06 F in tartrate.
(b) Iodine removed with thiosulfate.
(c) Solution 0.05 F in sulfosalicylic acid.
(d) Spatula tip full of Tiron added.

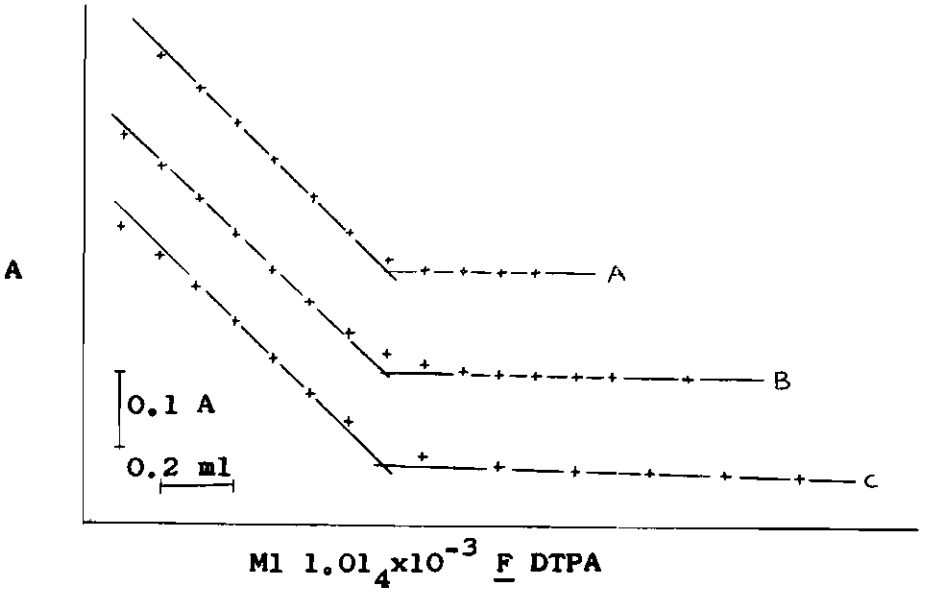

Figure 12

Influence of Cadmium Concentration on the End Point Region of the Titration Curve

A. Cd:Zn = 0; B. Cd:Zn = 1500
C. Cd:Zn = 3300

mask bismuth.

Cobalt, iron(II), manganese(II), nickel, and vanadate interfere by complete or partial cotitration. Iron(III) blocks the indicator. Gallium and indium appear to cotitrate, even in the presence of tartrate. The indium interference is not removed by chloride.

CHAPTER IX

THE DETERMINATION OF CADMIUM AND ZINC IN THE SAME SOLUTION VIA EDTA TITRATION

Introduction

It was reported in Chapters VII and VIII that zinc can be titrated chelometrically in the presence of large amounts of cadmium if the latter is masked with iodide in high concentrations. Those investigations were directed toward the establishment of the maximum cadmium:zinc ratios at which zinc could be determined with reasonable accuracy and precision employing visual as well as photometric end point detection. It is obvious that those methods could be combined with a separate titration of cadmium. Cadmium could also be determined by difference if the methods were combined with a titration of the sum of cadmium and zinc. Such procedures would, however, require two aliquots of the sample solution.

The present investigation has been directed toward the determination of cadmium and zinc in the same solution according to the following principle: At first, the sum of cadmium and zinc is titrated with a chelon. Potassium iodide is then added to the solution in an amount sufficient to mask the cadmium. Last, the chelon freed is titrated with a standard zinc solution.

EDTA was chosen as the chelon in the proposed method because it was known to serve well in the visual titration of zinc with

iodide masking of cadmium and because it is relatively inexpensive and readily available. Later experiments showed that neither EGTA, DTPA, nor CDTA offered any advantages over EDTA.

It is known that, in titrations of zinc and cadmium, Xylenol Orange can be employed as indicator up to a pH of about 6.5. In more alkaline solutions, the yellow color of the free indicator becomes reddish. Zinc can be titrated down to pH values somewhat below five while cadmium requires a pH of at least six to yield an acceptable end point(10). During the course of investigations to establish conditions for the sum titration, it was found that a pH of six or above was necessary for the titration if the Cd:Zn mole ratio in the sample was close to or greater than one. These facts indicate that, under the conditions specified, the Cd-Xylenol Orange complex is involved in some manner in the end point reaction and that it is necessary to perform the sum titration at a pH of about 6.1 where the indicator gives good end points for cadmium as well as zinc.

At pH six, however, difficulties were to be expected in the titration of the EDTA released when the cadmium was masked with potassium iodide. As was reported in Chapter VII, in solutions containing potassium iodide in high concentrations, the reddening of the free Xylenol Orange begins at a pH only slightly above five. Thus the titration of the sum and that of the EDTA released by masking of cadmium must be performed at different pH values. The sum titration is completed at pH 6.1-6.2; then potassium iodide is added and the pH lowered to about 5.0-5.5, depending on the iodide

concentration. It was found that exact measurement of the lower pH is not required. It is only necessary to add acid (preferably acetic so that the resulting solution will remain well buffered) until the reddish color of the free Xylenol Orange changes to a pure yellow. The free EDTA is then readily titrated with zinc solution to the appearance of the red color of the zinc-Xylenol Orange complex.

The reactions at both end points in this method are somewhat slow when the titrations are performed at room temperature. It was found that warming the solution to about 50° before beginning the sum titration removed the difficulty.

Since only moderate concentrations of cadmium are encountered in the present method, the extremely high concentrations of potassium iodide mentioned in the preceeding chapters are not necessary. Addition of potassium iodide to establish 30-40% w/v is usually enough to mask the cadmium completely. An insufficiency of iodide is indicated by a dragging color change before the end point. If such is noticed, the addition of more potassium iodide will restore the yellow color of the indicator and allow the titration to be completed to a sharp end point.

Equipment and Reagents

All equipment and reagents employed in this investigation are described in Chapter IV.

Procedure

Place the sample solution (up to about 100 ml), containing 5-110 mg cadmium and 3-65 mg zinc, in the titration vessel and

neutralize if necessary. Add 50 ml hexamethylenetetramine buffer pH 6.1 and one drop of 4 mg/ml Xylenol Orange solution. Heat the solution to about 50° and titrate to a yellow end point with standard 0.05 F EDTA solution. Add 30-40 g potassium iodide per 100 ml of the resulting solution, swirl to dissolve the potassium iodide, and then add 1:1 acetic acid (ca. 5 ml) until the yellow color of the indicator is restored. Titrate with standard 0.05 F zinc solution until the indicator color becomes noticably reddish; if the end point drags, dissolve in more solid potassium iodide and continue carefully to the sharp reddish end point.

Results and Discussion

Some representative results obtained with this method are listed in Table 5. The accuracy of the results is good and the precision is within 1-2 drops of the 0.05 F titrant solutions. It is, of course, possible to expand the ratios of the two metals beyond the limits given in Table 1. Then, however, the relative error in the result for the minor component becomes unacceptably large. This error is inherent in difference methods and can be reduced only by recourse to two separate determinations.

Table 5

Results of Titrations of Cadmium and Zinc in the Same Solution

Ml 0.00500 F Cd			Ml 0.00500 F Zn			Mole Ratio
Taken	Found	Diff.	Taken	Found	Diff.	Cd:Zn
23.80	23.81	+0.01	1.12	1.16	+0.04	21
22.19	22.13	-0.06	2.05	2.12	+0.07	10
12.16	12.18	+0.02	2.53	2.62	+0.09	5
19.38	19.38	0.00	5.08	5.12	+0.04	4
20.40	20.42	+0.02	10.14	10.18	+0.04	2
23.21	23.15	-0.06	23.03	23.14	+0.11	1
16.87	16.88	+0.01	26.39	26.47	+0.08	0.6
5.16	5.30	+0.14	25.90	25.89	-0.01	0.2
3.05	3.04	-0.01	33.31	33.35	+0.04	0.09
1.17	1.22	+0.05	23.28	23.29	+0.01	0.05

CHAPTER X

CONSTRUCTION AND EVALUATION OF A SEMI-IMMERSION PHOTOTITRATOR

Introduction

During the course of the work described in the preceeding chapters, certain limitations in the phototitrator became apparent. Since a more versatile phototitrator is not presently available (55,56), it was felt worthwhile to undertake the design and construction of a new instrument.

At first, it is desirable to consider the properties of an ideal, general-purpose phototitrator which would be applicable to any and all nonautomatic photometric titrations. The characteristics of such an instrument are discussed below; the order of listing does not reflect on the relative importance.

General: A photometric titrator should be highly stable, rugged, inexpensive, and as simple as possible. Reasons of expense and simplicity will restrict the consideration to a single beam instrument.

Light Source: In a single beam instrument, high stability of the light source is mandatory. Some means of adjusting the light intensity is desirable.

Titration Vessel: The titration vessel should be as simple as possible, preferably a piece of common laboratory glassware such

as a beaker. A selection of capacities is desirable. With a given vessel, it should be possible to change the length of the light path.

Monochromator: A reasonable degree of monochromacy is required. Interference filters usually are satisfactory but a means of continuously varying the wavelength is desirable.

Photodetector: The photoreceptor should be sensitive, stable, and capable of operation over the entire spectral region of interest. Linear response and absence of fatigue effects are required. The characteristics of the photodetector should not be affected by strong illumination, self heating, or moderate changes in ambient terperature.

Electrical Circuit: The circuitry should be as simple as possible and should be insensitive to ambient temperature changes and stray magnetic or electrical fields. Provision for scale expansion is mandatory with highly absorbing samples and in cases where the absorbance changes only slightly during the titration.

Photometric titrations are most frequently performed using a general purpose colorimeter, photometer, or spectrophotometer for the photometric measurements on the titration solution. It should be realized, however, that the requirements for a photometric titrator and a photometer, although similar, differ in several important respects.

Fluctuations in the readings cannot be tolerated in either instrument. Long term stability of the light source and electrical circuitry are important in a photometer but even more so in a phototitrator. Most photometers offer a means to easily recheck the 100

per cent transmittance setting. During a photometric titration, such checking is usually not possible; very often, for instance, the titration solution itself, in its initial state, is used to set 100 per cent transmittance. Consequently, in a photometric titrator, the 100 per cent setting must remain constant for at least the duration of one titration. A well designed double beam instrument will compensate for changes in light intensity, of course, but the complexity and expense of such an instrument can hardly be justified for titration purposes.

For a photometric determination, exact location of the zero and 100 per cent transmittance points is necessary; for a titration, the precise location of the 100 per cent transmittance point is unimportant so long as this location does not change during a titration.

In a photometer, the path length must be exactly reproducible from cell to cell and, frequently, the path length must be accurately known. On the other hand, the exact path length is never of interest in a photometric titrator and the only requirement is constancy during a given titration.

More differences could be listed easily but the items mentioned should serve to illustrate the contention that, in some respects, a photometer is inadequate for photometric titration purposes while, in other respects, a general-purpose photometer is too good an instrument to be diverted from its primary purpose and limited to service as a phototitrator.

It is true that a photometric titration can be carried out by

titrating in a vessel external to a photometer and performing absorbance measurements on portions withdrawn from the titration solution but such a procedure can be justified only for emergency or pedagogical purposes. To conveniently perform titrations with a photometer, it is nearly always necessary to modify the instrument. In most cases the first problem is the accomodation of the titration vessel, which is commonly much larger than the cuvettes for which the photometer has been designed. With the cell compartment modified or replaced, it is important to take care that the light beam is not defocused by the new vessel. Light tight introduction of the buret tip is necessary. The same holds for the stirrer or provision must be made beneath the cell compartment for a magnetic stirrer. Some workers have preferred to avoid major modifications by titrating outside the instrument and circulating the solution through a flow cell in the photometer, e.g. (57,58). The large minimum solution volume and the fixed pathlength of the cell are disadvantages of the method.

Further, few photometers have provision for scale expansion and any modification necessary to allow such an expansion is complicated, if possible at all. Perhaps the greatest disadvantage to the use of a modified photometer for titration purposes is the necessity for a light-tight cell compartment since such a compartment prevents direct observation of the solution for color changes, turbidity, positioning of the stirrer, bubbles, splashing, etc.

Many workers have successfully performed photometric titrations in modified commercial photometers, e.g. (25,59). It is clear,

however, that the adaptation of a photometer for titration purposes will hardly ever result in a fully adequate general-purpose photometric titrator. The construction of an instrument specifically designed for photometric titrations is the only solution if it is desired to fully enjoy the advantages of photometric titrations and to attain the widest latitude in operating conditions during research or routine analysis.

To permit easy operation and minimum restriction of vessel size and shape, the first consideration of the design is operation in ambient light. There are two principle approaches which permit such operation. The first is the use of chopped light to create an AC signal at the detector. This signal is electrically separated from the DC component due to ambient light reaching the detector. The AC signal can be amplified readily and, in fact, usually must be since low level rectification is difficult. The circuitry required is usually quite involved and prohibitively expensive for a simple titrator.

The second approach is based on the use of a relatively intense light beam which, after passing through the solution, is attenuated before striking the detector. This weakening of the light beam is accomplished by locating the monochromator between the sample and detector and, often, by the addition of a grey filter, grey wedge, or diaphragm. The light is attenuated by a large factor as is any ambient light which enters the detector housing. With appropriate design, the amount of ambient light then reaching the detector is negligible. Disadvantages of this approach are the

difficulty of obtaining a stable, high power supply for the exciter lamp and, in some cases, heating of the sample solution. The approach is often useful in automatic titrators, however, where long term stability is commonly not important since only large and/or sudden absorbance changes are utilized to trigger the relay mechanism.

A modification of this second approach has been employed by Flaschka and Sawyer (35). In their instrument, a rather weak, nearly parallel light beam passes through the solution and enters the detector compartment through an interference filter. The beam is then focussed on an extremely small photodetector without being additionally weakened. Only the light entering within a rather small angle can strike the photodetector and this angle is considerably less than that subtended by the light housing. Thus, only the ambient light which has been reflected by the titration vessel or scattered by the vessel or solution into this small angle need be considered. Further, the ambient light is white and only the small fraction which is passed by the filter strikes the photoreceptor; the amount of such light is negligible.

This device has been used for several years and has been found to be quite satisfactory in most respects. It is limited, however, in that no means of path length adjustment is available, other than the changing of titration vessels, and that only titration vessels with fairly flat and parallel sides can be used.

Consideration of and experimentation with a number of possible designs for photometric titrators have convinced the author that the

most versatile construction would be a complete departure from the usual practice. Instead of bringing the solution into the titrator, the instrument, or at least a part of it, would be brought into the solution. In principle, the light would enter the titration solution through a tube or light guide, pass through a length of solution, be reversed by a prism or mirrors, and leave the soltuion through a second tube which would lead to the detector. The combination of the two tubes and the prism (or mirrors) might be termed a photoprobe. By raising or lowering the prism, the light path length through the solution could be varied continuously. Application of one of the principles discussed above should provide insensitivity to ambient light.

Experimentation has shown, however, that it is difficult to construct a small photoprobe which is sufficiently rugged and unaffected by vibration; a completely satisfactory model has not yet been built. Agazzi (60) and Lacy (61) have constructed instruments whose designs point in this general direction. In both devices the ends of two tubes are immersed in the titration solution. A lamp is located near the immersed end of one tube; the light passes through the side of the tube and a short length of solution before falling upon the photoreceptor which is positioned behind a filter in the second tube. Neither model has provision for changing the path length although redesigning the tube mountings should make that possible within limits. However, changing of the filters is quite difficult and the titration of small volumes of liquids is impossible.

It was decided to attempt to build a simple, easily constructed semi-immersion instrument which would, nonetheless, be quite versatile. In this design, the light enters the titration solution from above through a tube whose immersed end is closed with a flat, transparent disc. The light then passes through a length of solution, leaves the solution through the bottom of the titration vessel, and enters the detector compartment. The tube through which the light enters the solution can be moved up and down to vary the path length. The principle of precise focussing on a small detector is again applied to exclude the influence of ambient light. In this design, freedom from the need for special cuvettes, operation in ambient light, and adjustability of the light path length are combined in a simple, inexpensive instrument. It is of interest to note that the principle of this design goes back to the well known Duboscq colorimeter and to the first really practical photometric titrator, built in 1928 by Muller and Partridge (62). In the latter device, a light bulb was suspended over a beaker containing the sample solution and the beaker was located immediately above the photodetector. As the instrument was used for automatic titrations, there was little need for path length adjustment and ripples on the surface of the solution were not troublesome.

Construction of the Phototitrator

The general features of the photometric titrator are shown in Figures 13 and 14.

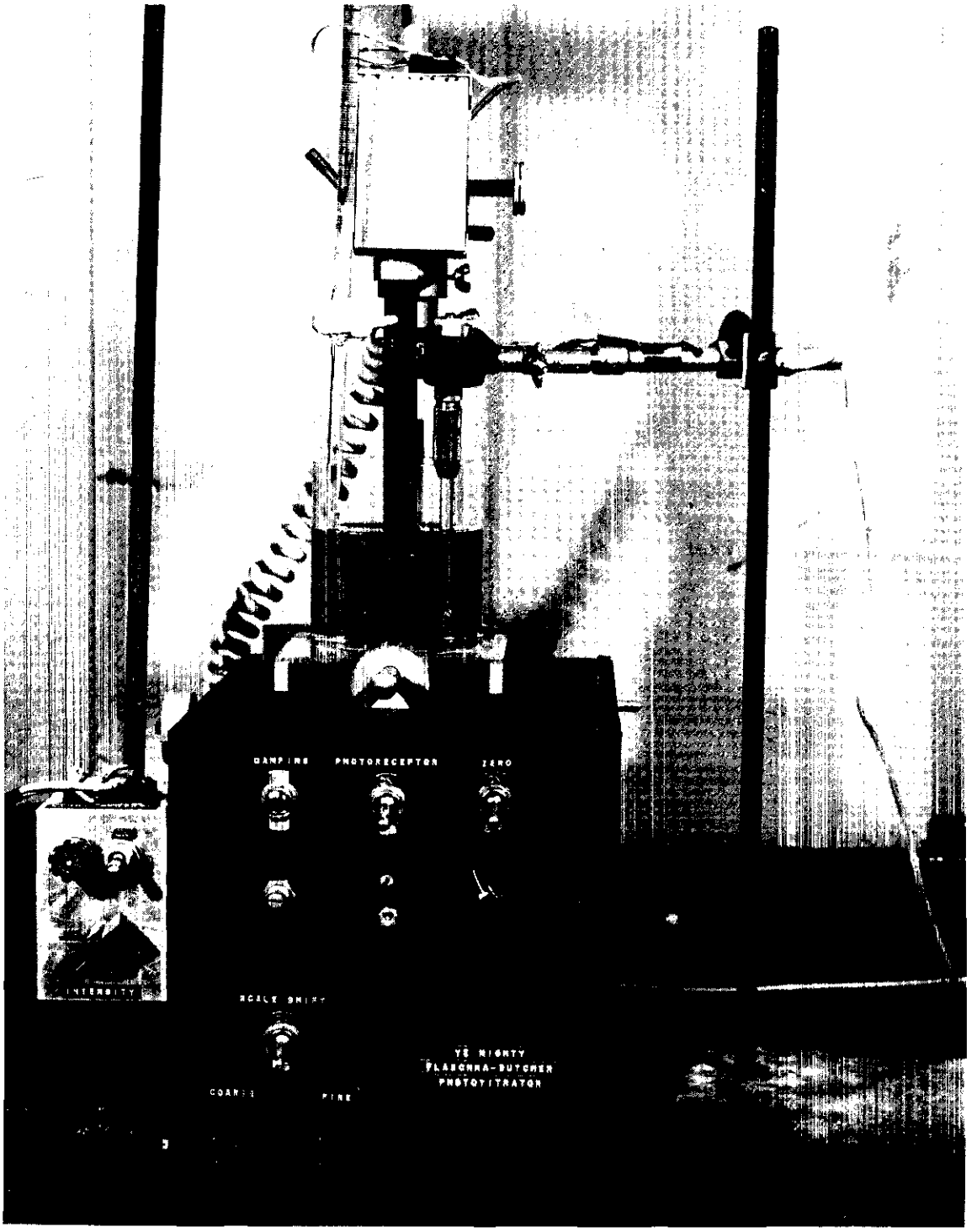

Figure 13

General View of the Assembled Phototitrator

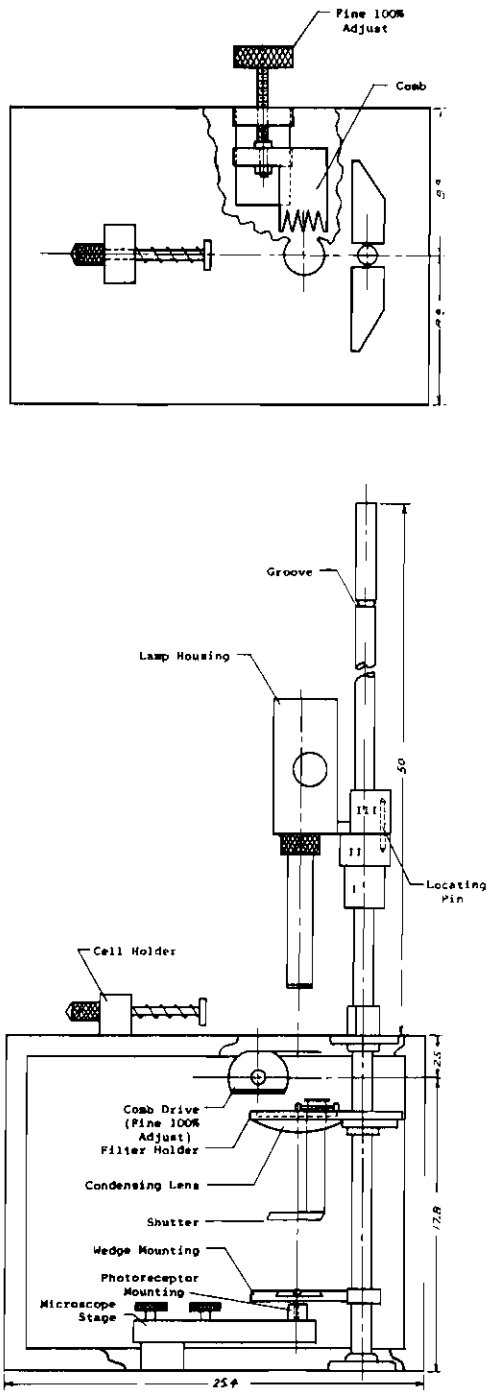

Figure 14

General View of the Assembled Phototitrator Side Door Removed

All dimensions in centimeters

The exciter lamp is a flashlight bulb (GE #222 or equivalent), operating at 3-4 volts and less than 0.5 ampere, and powered by a lead accumulator. This bulb has a small lens incorporated in the glass envelope. The bulb is mounted with this lens downward. A focussing lens (17.3 mm diameter, 12.5 mm focal length) is mounted on a rack and pinion to allow easy focussing. Both lamp and focussing lens are located inside the 1-5/8 x 2-1/8 x 3-3/4 inch housing (Catalog #CU-3001A, Bud Manufacturing Co.) shown in Figures 13, 14, and 15. The light beam passes downward into a glass or plactic tube which dips into the solution. The tube is blackened inside and closed at its lower end by a round plate cut from a glass microscope slide. The upper end of the tube is glued into a threaded brass fitting which screws into a tapped brass block which is epoxy glued into the bottome of the light housing. Tubes of different sizes and lengths are available and may be interchanged in a matter of a few seconds. A manually operated shutter is located in the lamp housing. This shutter provides a means of blocking the light beam when setting zero per cent transmission.

A vertical, half inch aluminum rod extends above the body of the titrator housing. Three brass fittings (denoted I, II, and III in Figure 14) are bored to give a sliding fit over the rod and are designed to permit the fixing of the location of the lamp housing. Fitting I is used for height (i.e. path length) adjustment and is fixed in place by tightening a thumbscrew against the rod. Fitting II can then be rotated about the rod to permit aligning of the light path; this fitting is then locked in place by a second thumbscrew.

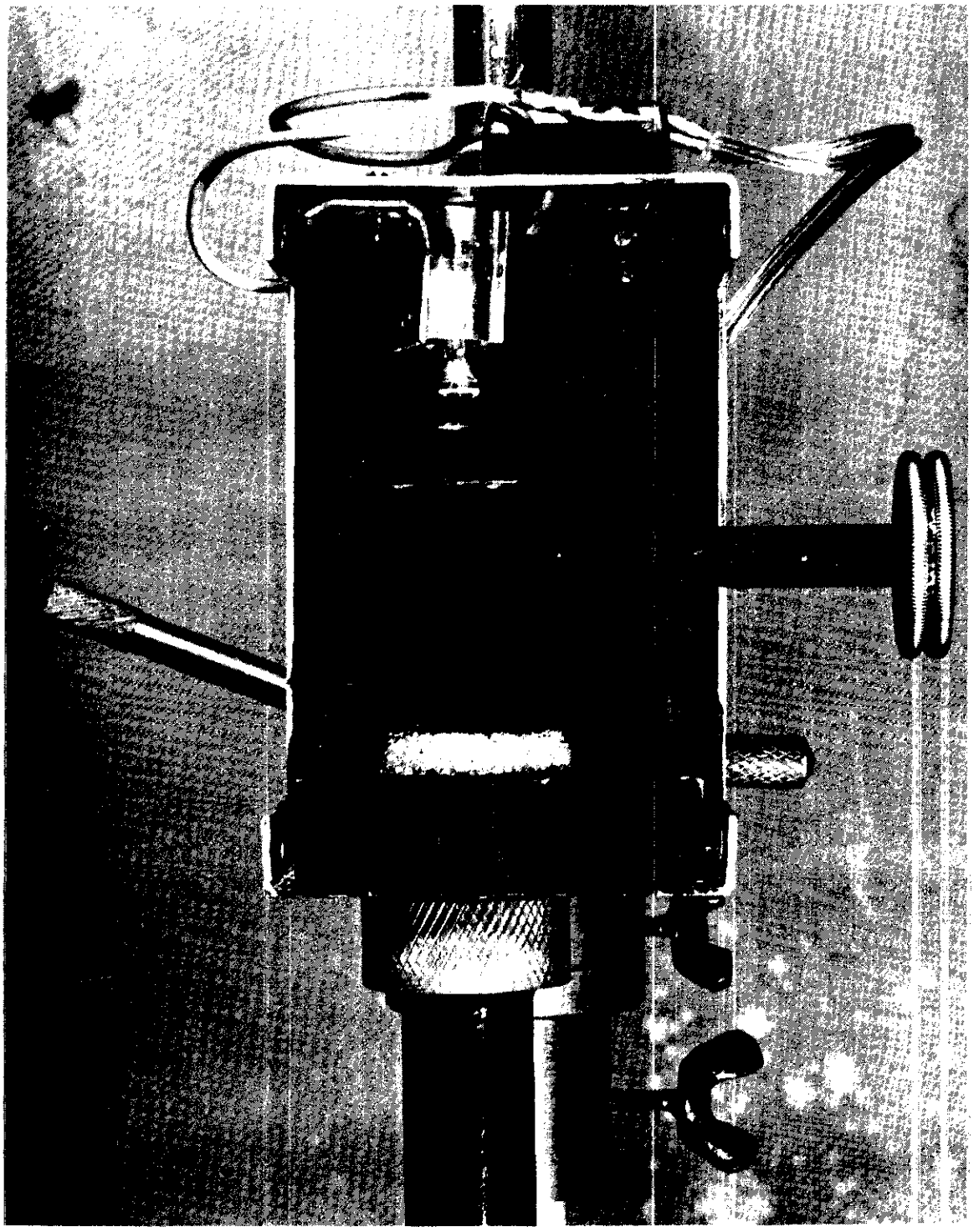

Figure 15

Interior Detail of the Lamp Housing

The lamp housing is attached to fitting III. A locating pin in fitting II fits snugly into a hole in fitting III to fix the position of the housing. A spring loaded pin in fitting III snaps into a groove near the top of the aluminum rod; this arrangement holds the lamp housing and tube out of the way while the titration vessel is being emptied and refilled.

The titration vessel can be a beaker; if a nonstandard size is desired, an appropriate container can easily be fabricated. A glass or plastic cylinder is glued (epoxy) to one side of a 10x10 cm glass or plastic plate and small plastic runners are glued to two parallel edges of the opposite side to prevent scratching of the plate. The spring-loaded cell holder presses the titration vessel against the brass blocks flanking the aluminum rod (See Figure 14). If the titration vessel is a beaker, a wood block with a "V" shaped notch is placed between the beaker and the cell holder to prevent sidewise motion of the beaker.

Stirring is accomplished by a small, glass propeller, dipping into the solution beside the light tube and driven by a miniature six volt motor (the stirring motor must not be powered by the lamp battery). The stirring assembly is mounted on a separate stand. If titration vessels with small diameter are used, stirring is effected by bubbling a stream of nitrogen through the solution near one side of the vessel.

The body of the instrument is a black, 7x8x10 inch steel box (Catalog #CU-879B, Bud Manufacturing Co.) having two removable sides. For ease of access, one side is provided with a piano hinge and a

latch. This box serves as the base for the vertical rod and as the enclosure for the filter, the photoreceptor, and most of the circuitry. The rod is fixed to the top and bottom of the box with Fisher "Flexaframe" feet. The light beam enters the box through a 20 mm (3/4 inch) hole located directly under the light housing.

The instrument has been built to receive interference filters as well as an interference wedge; either provides sufficient monochromacy, but the continuous wavelength adjustment, possible with the wedge, offers greater flexibility.

The filter holder shown in Figure 14 is milled from five mm (3/16 inch) brass plate and is mounted on a "Flexaframe" foot to allow positioning on the rod. The filter rests in a 5.1 cm (two inch) square recess in the holder and the light passes through a 4 cm (1-3/4 inch) square hole which is centered in the recess. A gravity operated shutter is located on the filter holder and is arranged to block the light beam when the filter is removed. A plano-convex condensing lens (60 mm diameter; 79 mm focal length) is attached to the borrom of the filter holder with epoxy glue.

In the alternative arrangement, a Bausch and Lomb interference wedge (63) is mounted in a holder similar to that of Safford and Westneat (64). The wedge is about 75 mm long and has a dispersion of 5.3 nm/mm. The peak transmittance is about 30 per cent and the half peak width (one millimeter slit) is about 10 nm. A pointer on the wedge is located above a millimeter scale which is fixed to the filter holder. The wedge holder has an adjustable slit (A fixed, one millimeter slit would be sufficient) and is mounted on

the vertical rod inside the instrument case. The slit is located in the smallest available portion of the light beam, i.e. as near the photoreceptor as possible.

If it is desired to use individual interference filters, the wedge is removed from its holder and the filter of interest is placed in the filter holder. When the wedge is to be used, an auxiliary cutoff filter is necessary (see below) and this filter is placed in the filter holder. If the wedge is expected to be the only monochromator, the shutter on the filter holder is unnecessary and can be omitted from the construction of the instrument.

A stripped down microscope stage (Catalog #F-3621, Lafayette Electronics, Syosset, N. Y.) is screwed to the inside bottom of the box. A brass heat sink, to receive the 1N2175 photoreceptor, is attached to the stage. By turning the two knobs on the stage, it is readily possible to bring the photoreceptor under the focus of the light beam.

The exciter lamp circuit is shown in Figure 16. The rheostat allows a coarse adjustment of the light intensity when setting 100 per cent transmittance. The rheostat and fixed resistor are located in a small housing on the outside of the body of the instrument so that the heat dissipated by these resistors will not affect the photodetector. An aluminum comb, mounted on a threaded drive mechanism (See Figure 14) is used for fine adjustment of the light intensity.

The 1N2175 silicon diffused photoduodiode (Texas Instruments Co.) is particularly qualified for the present application by its

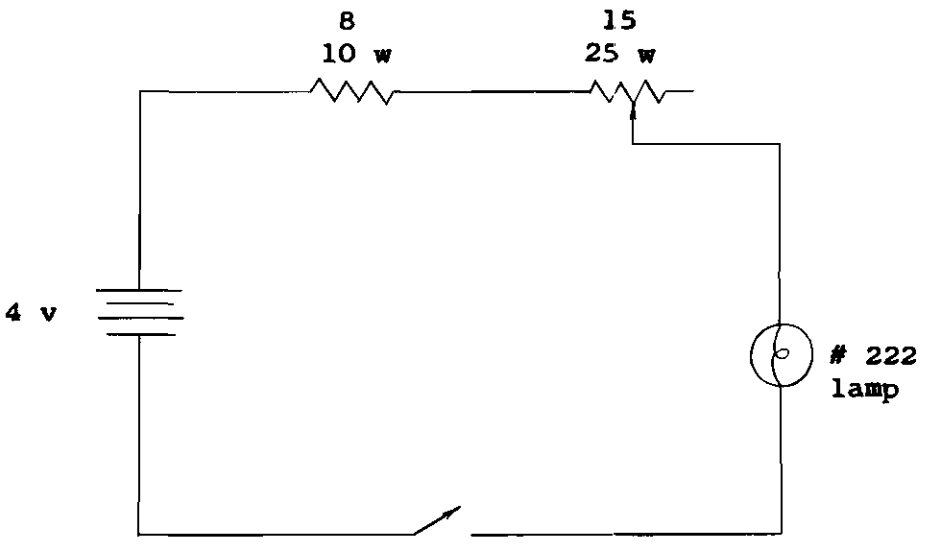

Figure 16

Exciter Lamp Circuit

extremely small size. The device is only 12 mm in length by 2 mm in diameter; the light sensitive area is less than one square millimeter. The 1N2175 is adequately sensitive (about 22 ua/mw/cm^2) throughout the visible region. The maximum sensitivity falls at about one micron; interference filters for use in the visible often pass near IR radiation so that additional filtering is necessary with this photoreceptor. The Texas Instruments LS-400 silicon photodiode is physically similar to the 1N2175 but is more sensitive (about ten times) and less affected by temperature changes. The unit tested in this laboratory was quite noisy, however, so the 1N2175 was used for the present application.

The 1N2175 photoduodiode requires a low impedance loan (10 kiloohms or less) if the current output is to be linear. A Rubicon galvanometer with a 100 division scale (Catalog #3434, Minneapolis-Honeywell Co., Philadelphia, Pa.) was found to be a suitable readout device. This galvanometer has an internal resistance of about 4.5 kiloohms, a sensitivity of about 0.0006 μa/mm, and a critical damping resistance of about 80 kiloohms.

The circuit shown in Figure 17 was designed for use with the 1N2175 and this galvanometer. Appropriate changes in the circuit would be necessary if a galvanometer with different characteristics were to be used.

The battery is a nine volt transistor radio battery (Eveready #226). At the low currents required (less than 0.1 microampere), this carbon-zinc battery is sufficiently stable and may be used instead of a mercury battery. Using a higher voltage battery will

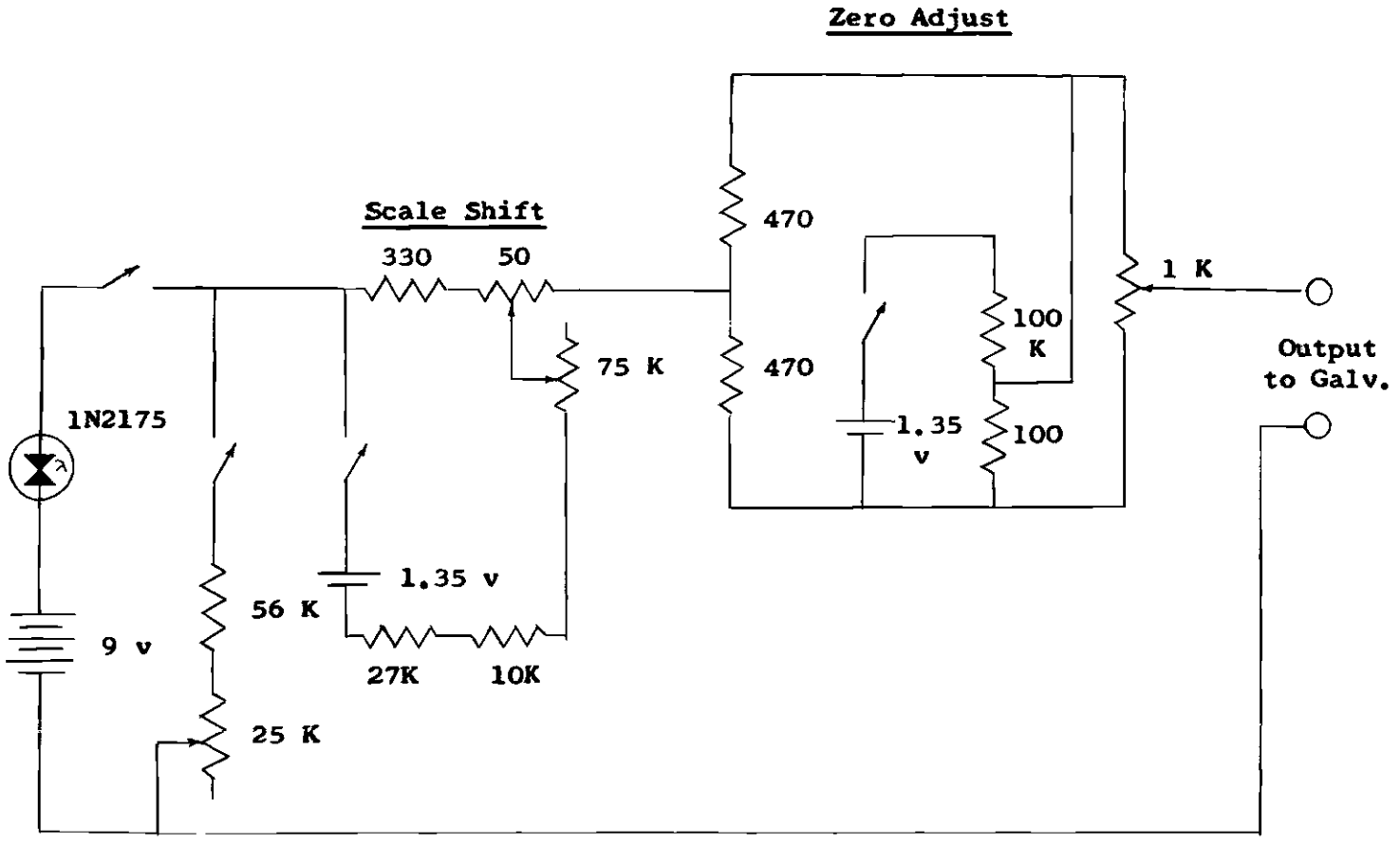

Figure 17

Photoreceptor Circuit

result in higher sensitivity (the 1N2175 is rated at 50 volts, maximum); more sensitivity than is provided by the nine volt battery is required only when titrating highly absorbing samples at wavelengths below about 350 nm.

The zero adjust portion of the circuit allows compensation for dark current and provides a simple, electrical means of adjusting the zero point at the galvanometer. The total resistance of this portion of the circuit varies from about 370 ohms to about 500 ohms as the control is rotated. This small change in resistance has a negligible effect on the damping and sensitivity of the galvanometer.

The scale shift portion of the circuit provides a means to shift the scale zero when high precision methods are to be used (21,65). With this circuit and the above galvanometer, somewhat above 400 scale divisions of zero suppression are available (depending slightly on the setting of the damping resistor). It is unlikely that more suppression will be required; if it should be, it can be obtained by shorting the 10 K or 27 K resistor. Small mercury batteries are used in both the zero adjust and scale shift circuits although 1.5 volt carbon-zinc cells would probably serve as well. The current drain in both circuits is low and battery life should be several years.

All controls and switches are mounted on the front panel of the instrument case. The controls are arranged so that all leads are as short as practical; this is done in order to minimize noise pickup. The batteries are mounted inside the case and near the

control panel. A shielded phone jack is located at the back of the instrument case for connection of the shielded galvanometer leads. The most noise-free operation was obtained with the galvanometer lead shielding connected to the instrument case, the case grounded, and the photoreceptor circuit floating.

Performance Tests

The instrument was tested to determine its insensitivity to external light, stability, and linearity of response.

Ambient Light: The effectiveness of exclusion of ambient light was tested by covering and uncovering the laboratory windows and turning the room lights on and off; no effect was noted. The apparatus was further subjected to the light of a 75 watt lamp, held above and about the light housing. The greatest effect observed was about 0.3 scale divisions, indicating that the light housing is sufficiently large to prevent most ambient light from entering within the critical angle.

Stability: Overall stability requires stability of the photoreceptor dark and light currents, the electrical circuitry, and the light source.

The dark current arises from a small conductance of the photodetector at zero illumination and is compensated by the zero adjust circuit. The stability of the zero reading is thus determined by the constancy of the dark current and of the current provided by the zero adjust circuit. In several experiments, the zero per cent transmittance point was found to suffer no short term fluctuations;

the maximum observed long term drift was about 0.2 scale divisions (on the 100 division scale) per hour. The scale shift circuit was tested by using the coarse (mechanical) adjustment on the galvanometer to set the pointer to about 100 scale divisions and returning the pointer to zero with the scale shift control. Again, no fluctuations were noted and the long term drift was less than 0.2 scale divisions per hour.

With the stability of the zero point assured, the stability of the light source and photoreceptor light current were investigated. Stability of the light source was achieved by operating the exciter lamp at low power levels (less than three watts) from a high capacity, well charged lead accumulator. At lower light intensities, the galvanometer drift from a preset transmittance value was negligible, indicating stability of both photoreceptor and light source. At the highest light intensities, a warmup period of several minutes was necessary; after that period, the drift was found to be about 0.5-1.0 scale divisions per hour and no short term fluctuations were noted. Since most photometric titrations are performed in a matter of five or ten minutes, this is adequate stability. If required, better stability can be obtained by using two batteries in parallel to power the exciter lamp.

Linearity of Response: With stability and insensitivity to ambient light established, the instrument was tested for linearity of response. From earlier work the galvanometer was known to be stable and linear so that it was necessary only to investigate the photodetector and associated circuitry, using the galvanometer for

readout. For the absorbance measured to be a linear function of concentration, it is necessary that, among other things, the indicated photocurrent (corrected for dark current) be directly proportional to the radiant power incident on the photocell. The testing of this linearity requires a means of increasing or decreasing the radiant power by known amounts. During this test, it is necessary that the relative intensities of all wavelengths of light reaching the photodetector be constant.

It was decided to perform the linearity test by decreasing the radiant power with screens. If the effect of diffraction at the wire edges can be neglected — as it almost certainly can — screens are perfectly grey in the spectral region of interest, i.e. they attenuate light equally at all wavelengths. The six screens available were calibrated by measuring their absorbances with a Cary Model 14 spectrophotometer. Then the transmittance (and thus the absorbance) of each screen was measured in the phototitrator. For each screen, the absorbance measured in the phototitrator was found to be higher than that measured in the Cary. If, however, the absorbance of each screen as determined in the Cary was plotted vs. the absorbance found with the phototitrator, a straight line with a slope less than one was obtained; a plot of this type is presented in Figure 18. An analogous plot of absorbance determined in the Cary vs. absorbance determined in a Bausch and Lomb Spectronic 505 gave another straight line having a slope somewhat greater than one. Changing the wavelength at which the absorbance measurements were performed had no effect on the results.

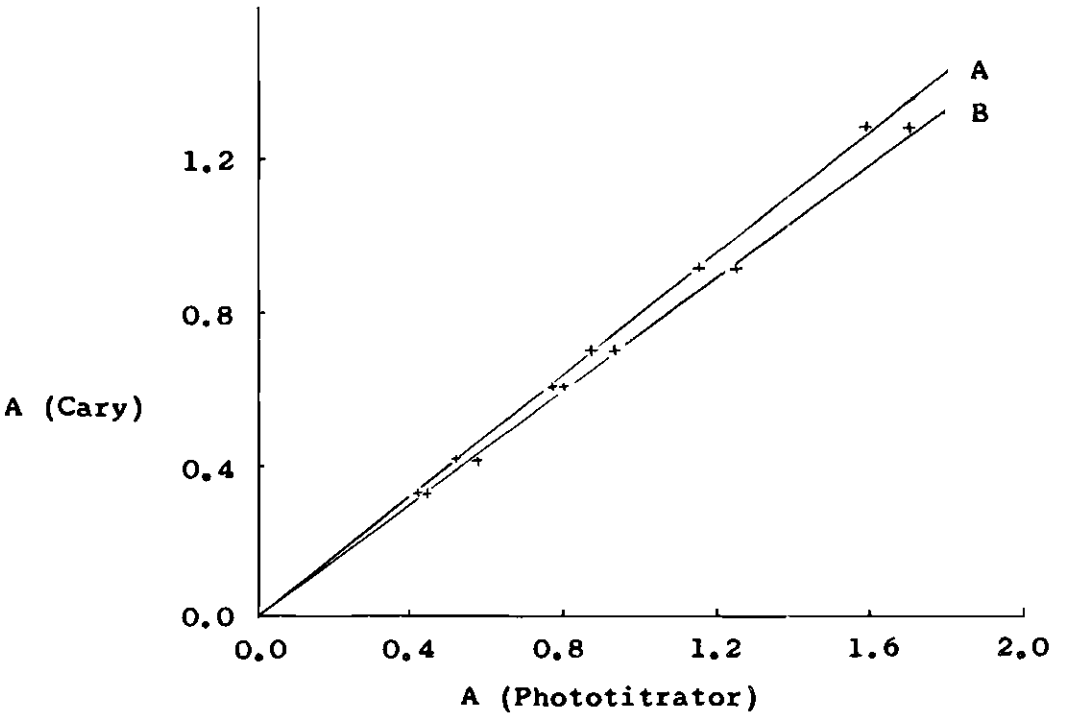

Figure 18

Effect of Increased Divergence of Light
on Measured Screen Absorbance

A. Filament image focussed on screen
B. Light beam defocussed (diverging)

For an explanation of the different slopes, consider a single wire of a screen, located between a light source and an aperture. Consider further the fraction of the aperture which is shadowed by the wire. When illuminated by parallel light, the wire and its shadow will have the same area per unit length. If however, the light is diverging, the fraction of the aperture shadowed by the wire will be increased, i.e. the absorbance of the wire will be increased. Likewise, if the light is converging, the absorbance will be decreased. As long as the whole aperture is illuminated and the screen wires are much smaller than the aperture, the measured screen absorbance will depend on the degree of convergence or divergence of the light beam; for a given focussing, the plot described above should be linear, however, if the instrument is linear. In order to test this explanation, advantage was taken of the ability to change the focussing of the phototitrator. The absorbances of the screens were determined under two conditions — first with the filament image focussed on the screen and second with the focussing lens moved away from the exciter lamp in order to obtain a strongly divergent beam. The results, presented in Figure 18, support the hypothesis. In both cases, linear callibrations were obtained. This was taken as a strong indication that the photodetector-galvanometer combination responds linearly.

With the stability of the instrument assured and the linearity of the response strongly implied, it was possible to examine the effects of nonmonochromacy.

The Bausch and Lomb interference wedge employs the second or-

der of interference. Thus, when set for 600 nm, the wedge also passes radiation of wavelengths 1200 nm and 400 nm, 300 nm, 240 nm, etc. Considerable nonmonochromacy errors were therefore expected, especially due to the passage of light at the first order wavelengths (i.e. in the near IR) where detector sensitivity is at a maximum and where maximum radiant power is emitted by an incandescent lamp.

Experiments were performed in which successive increments of a colorant solution were added to a solution in the titration vessel and absorbance at the wavelength of maximum absorptivity of the colorant was followed. The colorants and solutions were selected so that equilibrium effects would not produce curvature in the plots of absorbance vs. volume of colorant added. An infrared filter and several band pass filters were employed to attenuate, respecitvely, the first order IR radiation and the third and higher order blue and near UV radiation. The curves obtained, with and without these filters in the light beam, are shown in Figures 19 and 20. All absorbance readings were corrected for dilution. From these curves, it is clear that the interference wedge monochromator, in conjunction with auxiliary filters, provides sufficiently monochromatic radiation for photometric titration purposes so long as the absorbance of the sample is below about 1.0. The #4600 Corning IR blocking filter used does not cut off completely below about one micron; the use of an IR filter which is opaque down to nearly 700 nm would probably allow an extension of the linear range, especially for work at lower wavelengths. Since an IR filter is needed in most work, it

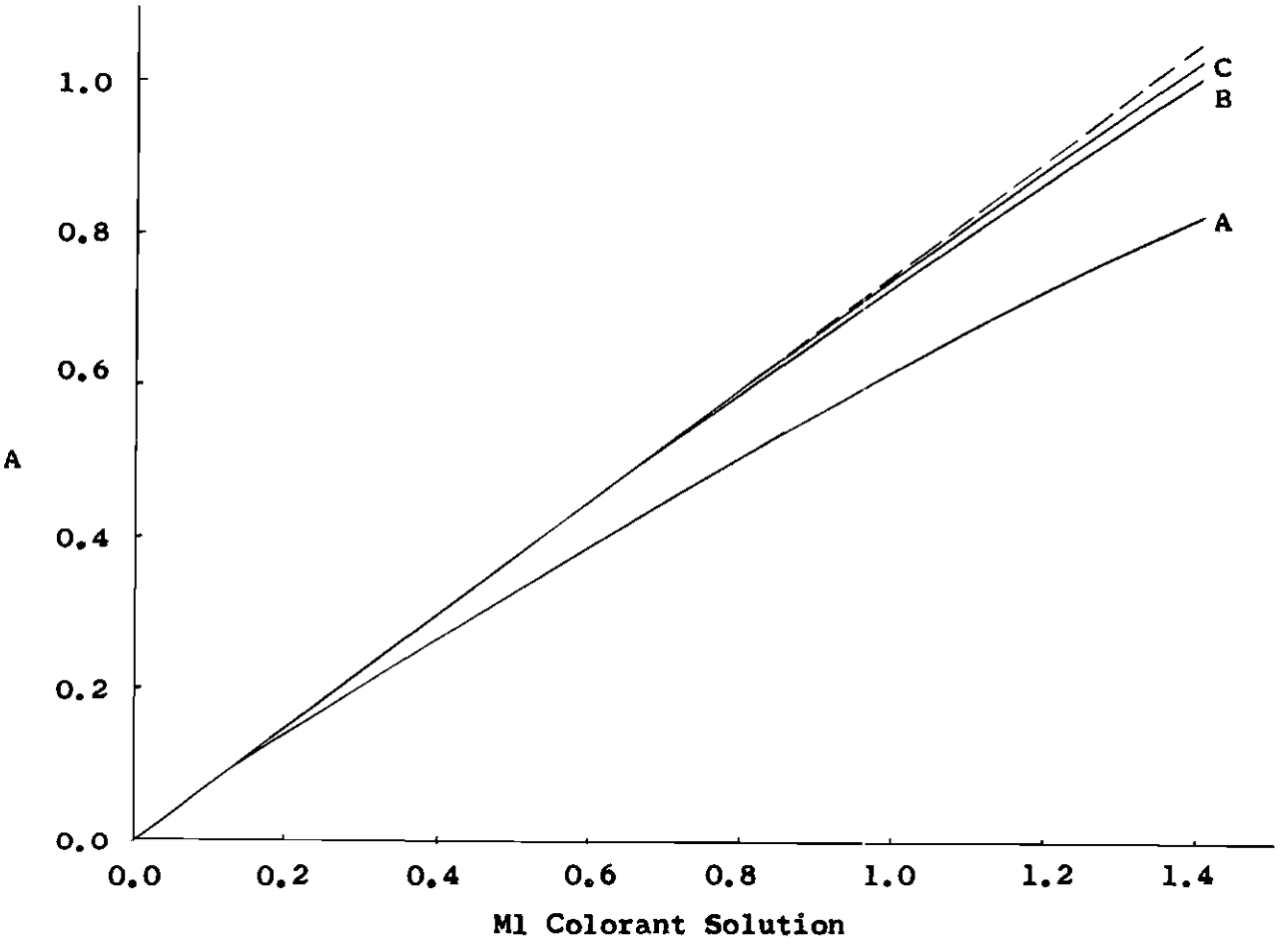

Figure 19

Monochromacy Test

$CuSO_4$ added to ammonia buffer pH 10 Solution
Interference wedge set at 630 nm

A. Wedge alone
B. Wedge + Corning #3486 yellow filter
C. Wedge + Corning #3486 + Corning #4600 IR filter

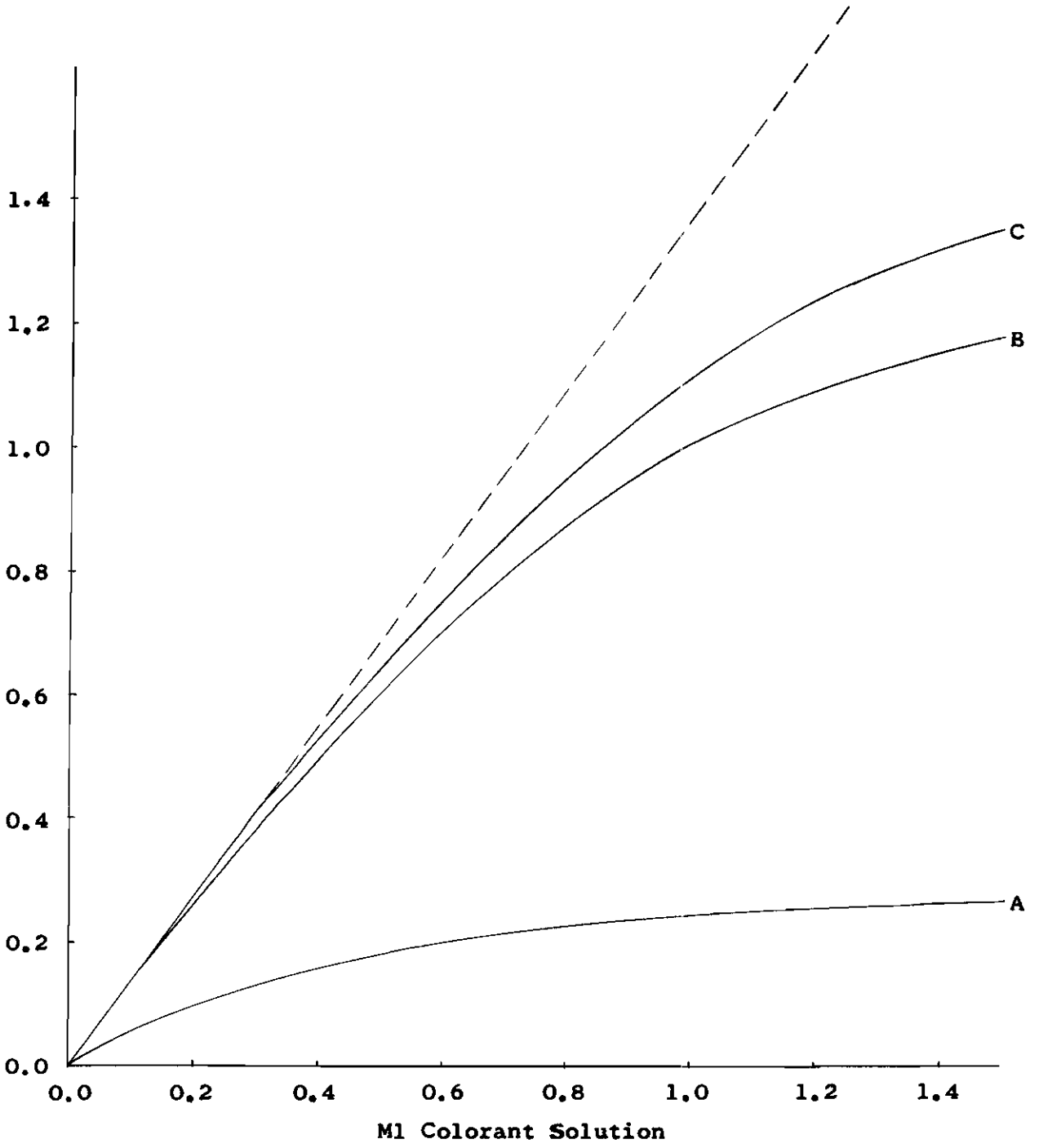

Figure 20. Monochromacy Test

Methyl Orange solution added to ammonium acetate solution (pH 7)
A. Wedge alone, set at 466 nm
B. Wedge + Corning #4600 IR filter
C. Wedge + IR filter + Corning #5031 blue filter

is convenient to glue one to the inside of the light entrance hole of the instrument case. This placement of the filter also aids in preventing the entrance of dust.

Titrations can often be performed in the nonlinear absorbance range if the absorbance change during the course of a titration is small. This is due to the fact that, within a short portion of a curve, linearity is closely approximated. Titrations with step indication can often be performed in the nonlinear range since only a small portion at the beginning or end of the step is utilized to detect the end point and, again, linearity is sufficiently approximated.

Calibration and Alignment

The interference wedge must be calibrated before being put into use. For the wedge in the present instrument, this was done with the aid of the strong mercury emission lines of a fluorescent lamp at 435, 546, and 578 nm. The lamp, when viewed through the wedge, produces three bright lines, corresponding to those wavelengths. Each line was centered, successively, in the one millimeter slit and the corresponding reading on the scale which is mounted on the filter holder was noted. Since the wedge is linear (63), the data were then fitted to a straight line to obtain the calibration.

$$\text{Scale Reading (cm)} = \frac{758 - \text{wavelength (nm)}}{53.3 \text{ (nm/cm)}}$$

The alignment of the optical system is accomplished as follows:

with the path length set at several centimeters, the exciter lamp is turned on and the focussing lens is moved via the rack and pinion drive until a filament image is focussed at the top of the instrument case. The light housing is rotated until the image is centered in the entrance hole on top of the case (the image is made visible by placing a piece of tissue paper over the hole) and the housing is then fixed in place by means of the appropriate thumbscrew. The wedge monochromator is rotated until the light beam is centered in the slit and is also fixed in place. Next, by raising or lowering the filter holder, the condensing lens attached to it is brought into the position such that the smallest spot of light is obtained in a place level with the top of the photocell; the filter holder is then fixed firmly in place with its set screw. The position of the condensing lens and wedge holder may be left unchanged thereafter. With the lamp and photoreceptor on, the focussing lens and microscope stage are successively adjusted until maximum galvanometer deflection is obtained. The optical alignment if then complete.

When the light path length has been changed, for realignment of the system it is usually only necessary to rotate the light housing until maximum galvanometer deflection is again obtained. If the path length change is large or if a new titration vessel is inserted, it may be necessary to touch up the adjustments of the focussing lens (rack and pinion) and photocell (microscope stage).

Operation

Zero per cent transmittance is set by closing the shutter in

the light housing, turning on the zero adjust circuit, and turning the zero adjust control until the galvanometer pointer is at zero scale divisions. To set 100 per cent transmittance, the reference solution is placed in the titration vessel, the shutter is opened, and the light control rheostat is adjusted until a reading near 100 scale divisions is obtained. The fine adjustment is then performed with the comb. If a suppressed zero is required, zero and 100 per cent transmittance are set exactly, the zero suppress circuit is turned on, and its controls are adjusted to return the pointer to zero. Zero per cent transmittance is then at -100 scale divisions. Next, the rheostat and comb are used to reset 100 per cent. More zero suppression can be obtained by repeating the process.

APPENDIX

GLOSSARY OF COMMON NAMES AND ABBREVIATIONS

Chelons

CDTA: (1,2-cyclohexenedinitrilo)tetraacetic acid

DTPA: (diethylenetrinitrilo)pentaacetic acid

EDTA: (ethylenedinitrilo)tetraacetic acid

EGTA: [ethyleneglycolbis(nitriloethyl)]tetraacetic acid

Indicators

Calmagite: 1-(6-hydroxy-m-tolylazo)-2-naphthol-4-sulfonic acid

Murexide: ammonium purpurate

Tiron: 4,5-dihydroxy-m-benzenedisulfonic acid (usually the disodium salt)

Xylenol Orange (XO): 3',3"-bis([bis(carboxymethyl)amino]methyl)-5',5"-dimethylphenolsulfonphthalein

Zincon: o-(2-[α-(2-hydroxy-5-sulfophenylazo)benzylidene]-hydrazino)-benzoic acid

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In February, 1963, he was married to Mary Driver Murray of Hollywood, Georgia.